

A TRIDENT SCHOLAR PROJECT REPORT

NO. 265

The Use of Thermal Spraying to Enhance the
Bonding Characteristics of a Urethane Coated Propeller



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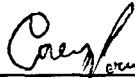
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**The Use of Thermal Spraying to Enhance the
Bonding Characteristics of a Urethane Coated Propeller**

by

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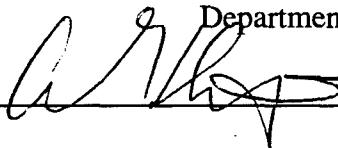


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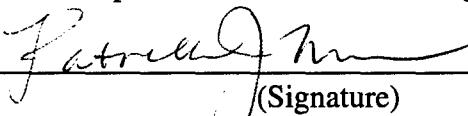


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ABSTRACT

In order to reduce the cost and machining time of producing propeller blades, the Naval Surface Warfare Center, NSWC, has developed an alternative production method for propeller blades. The alternative production method consisted of a Nickel-Aluminum-Bronze (NAB) blade, covered by two coats of paint and a urethane coating. After exposure to seawater and impressed current cathodic protection, the bond between the paint and the NAB substrate failed to meet NSWC's minimum required bond strength of 80 lbs./ linear inch.

This project attempted to improve the bond between the paint and NAB by developing a surface treatment technique that would produce a strong, lasting bond. The surface treatment technique chosen was thermal spraying, specifically arc wire spraying, which created a rough, porous surface. This type of surface promoted mechanical bonding, as well as enhanced chemical bonding, of the paint to the substrate. In order to produce various surfaces, the thermal spray distance was varied at six inch intervals from six inches to two feet. A 90-degree peel test, SEM analysis with x-ray micro-analysis, and optical metallography were all used to evaluate the characteristics of each coating.

After testing, it was determined that flame sprayed coatings created a surface that produced a mechanical bond, increased chemical bonding, and reduced the effects of cathodic protection.

KEYWORDS: Propeller Blades, Urethane, Thermal Spraying, Mechanical Bonding

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INTRODUCTION

Submarine propellers have become very time consuming and expensive to produce. The specific requirements for acoustic performance, speed, and robustness, make the design and manufacturing of these propellers a very complicated process. As submarine technology has increased, so has the need for quieter and more efficient propellers on submarines. This is no better evidenced than in the Navy's newest submarine, the SSN-21 SEAWOLF. This submarine is currently the fastest, quietest, and most lethal attack submarine in commission. With this improved performance comes cost. In order to meet the acoustic, hydrodynamic, and performance criteria required by the new SEAWOLF Class submarine, each specially designed propeller system costs approximately 40 million dollars, as compared to only two to three million dollars for the propeller system of the current LOS ANGELES Class Attack Submarine.¹ Additionally, a similar high cost propeller system will be used on the VIRGINIA Class submarine, the follow-on to the SEAWOLF. This increase in cost is due to the high amount of post-cast machining that is required to bring each individual blade to within the dimensional tolerances required. These new propeller systems are produced blade by blade, and then assembled around a hub by using sophisticated laser positioning equipment.

The current method for propeller production is to pour the molten metal, Nickel-Aluminum-Bronze (NAB), into an oversized sand mold of the propeller blade to be produced. The sand cast is generally 0.25 to 0.50 inches larger than the final blade dimensions. This is done to allow for the common errors which occur in the sand mold process to be corrected by high precision milling. If the sand cast was produced at the

exact required size, no errors would be allowed in the casting process, a feat that is nearly impossible.

After solidifying, the blade is removed from the mold and placed in a multi-axis milling machine where it is machined to its final shape. Final inspection of each blade is performed by a Coordinate Measurement Machine, (CMM), ensuring that the blade is within the required, and highly precise, design dimensions. This process is extremely expensive and time consuming, and is repeated for each blade produced.²

A new, more economical, and less time consuming approach to propeller production has been under development at the Naval Surface Warfare Center, Carderock Division (NSWCCD). The new process proposed by NSWC involves three steps.

The first step is to undercast the blade by approximately 0.125 in. using traditional sand casting techniques. The blade is undercast so that the highly precise final dimensions can be later achieved by carefully casting an outer layer of urethane around the blade.

The second step is to paint the blade after removal from the sand mold. The blade is painted for two specific reasons. The primary reason for painting the blade is that the paint acts as the adhering agent for the urethane. Without the paint the urethane would not be able to adhere to the metal blade and thus this new system would not work. Additionally, the paint provides additional corrosion protection for the propeller blade.

The third and final step is to place the painted, undercast blade into a second mold and inject urethane into the mold. The second mold was produced by NSWC within the specified dimensional tolerances required by the blade. The urethane surrounds the blade in the mold, and after curing, produces a final blade that meets all dimensional required.³ The only machining now required is the milling of the palms of the blades, which are used for locating the blades.

Such molds have been used to produce over 20 blades each, thereby greatly reducing the post sandcast cost and machining time. The mold used by NSWC, and a final blade cast from the mold, can be seen in Figures (1) and (2) shown on the following page.

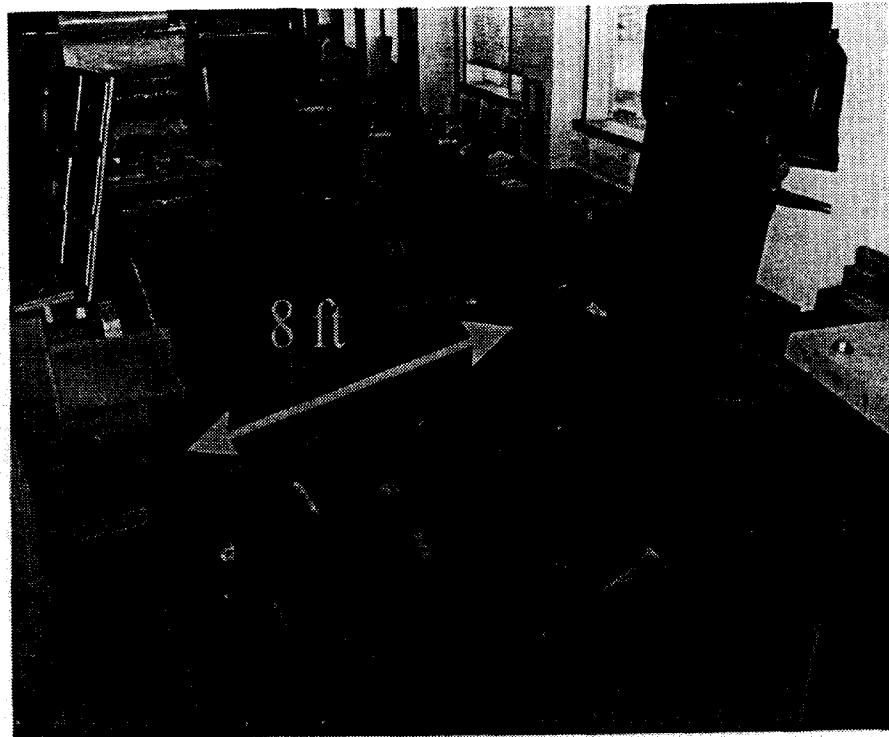


Figure 1 - Mold used by NSWC to produce a urethane coated propeller

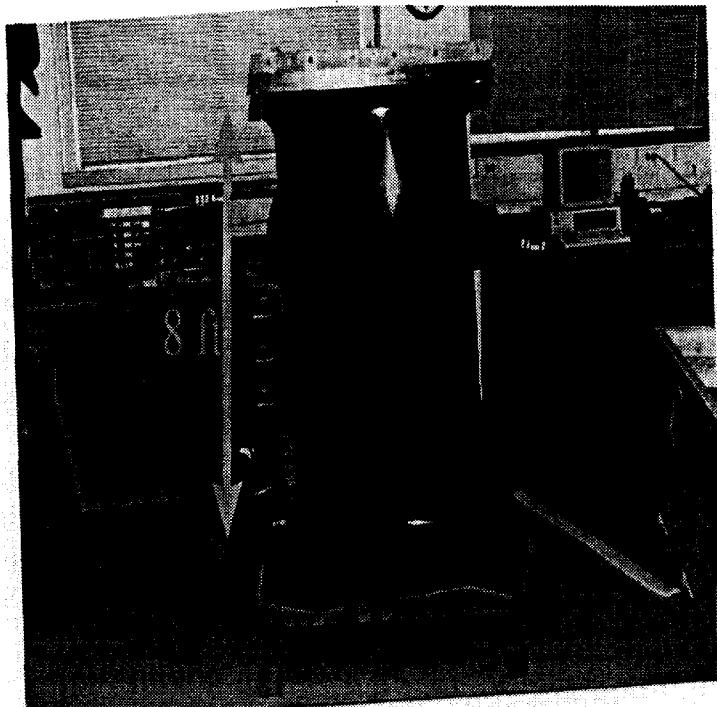


Figure 2 - Urethane coated propeller produced by NSWC-Carderock from mold in figure 1

These molds allow for the urethane to be easily controlled in the coating process, thereby producing a blade with the desired final dimensions at a low cost. This experimental process reduced the machining time for each blade by 90% and the cost by approximately 50% from the traditional production method.⁴

To date NSWC, Naval Surface Warfare Center, has only evaluated this process using HY-80 steel, as the metal substrate of the system. This Trident Scholar project is extending NSWC's research by using the previously untested NAB, Nickel-Aluminum-Bronze, as the substrate. NAB was tested since it is the Navy's choice for producing propeller blades due to its acoustic performance and corrosion resistance.

As with all experimental procedures, problems arose with the method proposed by NSWC. The critical requirement of NSWC's process was that the urethane adhere to the paint, and that the paint adhere to the metal substrate. After testing, it was found that an adhesion problem developed between the paint and the metal substrate. The problem developed after exposure to seawater environment with a cathodic protection system similar to the one used on the SEAWOLF submarine. When debonding of the paint from the substrate occurred, the urethane coating would debond from the blade since it chemically adhered to the paint. This caused the blade to lose the physical attributes that allowed it to achieve the hydrodynamic and acoustic properties required by the submarine.

This Trident project investigated whether or not a mechanical bond, and enhanced chemical bonding, could be created to overcome, or inhibit, the degradation of the bond that occurred between the paint and substrate when exposed to cathodic protection. In order to create a mechanical bond, a rough surface with high porosity needed to be created at the paint - substrate interface. Thermal spraying was used to create a rough surface on the

substrate. The thermally sprayed coating was applied at varying distances to create multiple test samples with varying surface characteristics. Paint was then applied to the surface of each sample, followed by a urethane coating in order to simulate the exact composition of the propeller blade surface. Each sample was then placed in seawater under cathodic protection for specified time periods. Each spray distance was then evaluated using a 90-degree peel test, and compared to the performance of non-sprayed samples that were exposed to the same conditions. Optical microscopy and SEM analysis using x-ray micro-analysis were used to evaluate the surface characteristic created by the thermal spray.

The overall objective of this project was to determine if the thermal sprayed coatings could provide an acceptable mechanical bond, and enhanced chemical bond, between the paint - NAB interface, and if so, which spray distance provided the best surface characteristics and performance over extended exposure to seawater and cathodic protection. If successful this project will overcome the final obstacle encountered by NSWC in their research, thereby making this new production method a viable alternative to the current production methods of submarine propeller blades.

BACKGROUND

PRIOR WORK

NSWC has constructed and tested multiple urethane coated propeller blades made of HY-80 steel for wear, bio-fouling, and environmental behavior. Small test specimens, prepared by NSWC as previously described, were placed on both the USS TREPANG (SSN 674) and Tugboat "Tilly", in New York Harbor.⁵ These specimens were not tested under cathodic protection, rather they were evaluated to determine the effects of long term environmental exposure on the material properties of urethane. The urethane characteristics evaluated were bio-fouling, wear properties, and the overall condition of the urethane after open water operation. The urethane was found to possess outstanding bio-fouling resistant properties, as well as good wear resistance. The open water environment had no effect on the properties of the urethane. Additional tests successfully completed by NSWC were cavitation, shock, abrasion, impact resistance, acoustic, dimensional stability, thermal / mechanical cycling, and hydrolytic stability testing. The success of these tests proved the viability of using urethane as the surface material of a propeller blade.

Additionally, adhesion testing was performed by NSWC under cathodic protection to determine the effects of this anti-corrosion system on the properties of urethane and paint. After completing this test, it was found that cathodic protection caused an adhesion problem between the paint and metal substrate. This indicated, that although the urethane possessed acceptable material properties, the bonding characteristics of the urethane and paint under cathodic protection did not meet NSWC's design criteria.⁶ The bond failure indicated that the paint was the weakest link of the propeller system. Although the weakest link in the new

propeller system, the paint was also the most essential element of the propeller system because the urethane could not adhere to the blade surface without it. Due to the vital importance of the paint in this system, NSWC investigated various paint systems.

NSWC applied the paint to the top of the metal plate to act both as corrosion protection for the metal test specimen, and as the adhering agent for the urethane. The paint must adhere both to the metal, and to the urethane extremely well. Finding a paint with this property, and the ability to resist corrosion, has proven very difficult. Paints are designed to perform specific functions, such as adhesion or corrosion resistance. Many different paints have been tested by NSWC and none have proven to meet all the above requirements. The initial paint system used by NSWC was a 2842-1109 primer and 2842-1110 final coat.⁷ This paint was designed to function as a strong adhesive between objects and thus its initial bond strength was high. Initially the paint adhered to the urethane with a peel strength of over 200 lbs / linear inch of peel, well above the required strength. After approximately one month under cathodic protection, the paint would debond under a 10 - 30 lb. load and thus the system failed.⁸ The second system evaluated consisted of Military Standard 150 series paint for both layers. The MP-150 series paint was designed for use on ship hulls and its primary characteristic is its resistance to cathodic protection. Contrary to the 2842 series paint, the MP-150 paint was not a strong adhering agent, especially in shear which is how the peel test is conducted. The MP-150 paint adhered to the plate moderately well under cathodic protection, but its initial peel strength to urethane was under 30 lbs. / linear inch of peel. Therefore, it did not meet the design criteria of the project.⁹ A third system was attempted by using the Military Standard 150 paint as a primer, and the 2842-1109 as the final coat in hopes of having the primer adhere to the plate and the 2842-1109, while the

2842-1109 adhered to the urethane. By using this method, it was hoped that the corrosion resistance properties of the primer would protect the 2842 paint and that the adhesion properties of the 2842 paint would maintain the overall bond integrity of the system. This system failed with an initial peel strength of 30 to 45 lbs.¹⁰ After careful evaluation of the three systems by NSWC, it was determined that the best system to test the thermal spray coating on would be the 2842-1109 / 2842-1110 paint system.

NSWC had not evaluated NAB as a substrate material for a variety of reasons, including adhesion concerns between the NAB and paint, costs, and time obligations to other research areas. NSWC focused primarily on research into the adhesion of paint and urethane to HY-80 steel when attempting to develop the urethane coated propeller. Preliminary investigations by NSWC indicated that adhesion to bronze would be difficult, therefore, bronze was never investigated by NSWC. This Trident Scholar project consisted of two phases. First, it extended NSWC's research to NAB, the actual submarine propeller blade material. Second, this project developed a surface treatment technique that would allow for adhesion to bronze and would reduce the effects of cathodic protection on the propeller system.

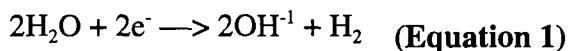
CATHODIC PROTECTION

On the SEAWOLF submarine, two distinct metals, the steel hull and NAB propeller system, are immersed in sea water. The metals and alloys that make up the SEAWOLF corrode in seawater. In order to reduce this corrosion rate, the potentials of the metals can be lowered to a more negative value. This can be accomplished by electrical means by using impressed current cathodic protection. The corrosion rate can also be reduced by applying

various coatings, such as paint, to the exposed metal. On the SEAWOLF submarine, a paint coating is applied to the propeller system and hull in order to slow the rate of corrosion. Coatings alone are not enough to greatly reduce the corrosion rate, thus an additional protection system is required to protect the exposed metals.

One system commonly used to inhibit corrosion is impressed current cathodic protection. Impressed cathodic protection, ICCP, is an electrical circuit with a DC power supply on board the ship. In this circuit, the ship acts as one electrode, and another isolated electrode is placed into the water and connected to the power supply to complete the circuit. The principal by which ICCP works is that it lowers the potential of the steel hull and the other metallic components connected to the hull to -0.850V referenced to a Ag / AgCl electrode, thereby reducing the corrosion rate of the hull and connecting metals. The lower the ICCP system forces the potential of the metals, the further their corrosion rate is reduced.¹¹ If the ICCP system reduces the potential too low, hydrogen embrittlement will occur, causing the paint to debond from the NAB and/or the NAB substrate to crack. To improve the effects of the ICCP system, a coating can be applied to the protected surface to insulate it from the electrolyte solution. These coatings degrade over time, but the ICCP system still functions without the coating. Locations of coating cracks, voids, and failures can serve as a corrosion concentrator on the ship, even with the ICCP system.

One problem with the ICCP system is that the potential to achieve an acceptable amount of corrosion in the system is very near to the potential where water is electrochemically reduced, -0.850 V in reference to a Ag / AgCl electrode. The potentials of the various metallic components of the ship will vary somewhat and may be reduced low enough to chemically reduce water according to the reaction in Equation (1).



In order for this to occur, the metal must come in contact with the water, and since both urethane and the paint are porous materials, the NAB eventually comes in contact with water. When this contact occurs, the water can be reduced and hydroxyl ions can be produced at the paint substrate interface.¹² In the current system, the sea water eventually seeps through the urethane coating and the paint and comes in contact with the NAB substrate. "The liberated OH⁻ ions probably play an important role in undermining the film in view of the well-known ability of alkalies to destroy the bond between paints and metals."¹³ "Hydrogen evolution, even in neutral or alkaline solutions, destroys coatings and produces various forms of hydrogen damage."¹⁴ This is the suspected reason for the eventual failure of the bond between the paint and the metal substrate, as well as the bond between the paint and urethane, after environmental exposure under impressed current cathodic protection.¹⁵

THERMAL SPRAYING

In order to overcome the destruction of the chemical bond due to cathodic protection, various methods of creating a mechanical bond, or an overall stronger bond, were investigated. Theoretically, the hydroxyl ions attack the chemical bond between the paint and the substrate, but should not attack the mechanical bond between the two elements. Also, increasing the surface area would lessen the hydroxyl ion influence on the bond between the paint-NAB interface. After reviewing multiple surface treatments, thermal spraying was chosen because it is an efficient, economical, and simple way to create a rough, porous surface on the substrate that would allow for an effective mechanical bond to be created

between the paint and NAB surface.

There are many types of thermal spraying processes ranging from powder spraying (the traditional approach), to the improved arc wire spray system. Through many technological improvements, the arc wire spray system has surpassed the plasma (powder) spray system, and now has many advantages over powder spraying. In arc wire spraying (AWS), the feedstock is completely melted, while in plasma spraying (PS) the system relies on placing a range of particles into the center of a flame and keeping them there long enough to produce particles in the plastic state. Arc spray only requires air and electricity, while PS requires gases such as hydrogen, nitrogen, and argon which are expensive and dangerous. AWS produces a consistent coating and pattern every time when using the same setup, while coating consistency is a major problem with PS. AWS also produces higher bond strengths to the substrate material than does the PS system.¹⁶ The spray time and machining time are much quicker in AWS, due to its simplicity of set up and higher spray rates. The AWS system is twenty percent of the cost of a PS system, \$20,000 versus \$100,000 for a new system, and costs one ninth of the amount to operate a PS system.¹⁷ In AWS, the bond strength of the coating does not change as the angle of spray varies from 30 to 90 degrees, while in PS, the angle of attack greatly effects the coating bond strength. Finally, the AWS system produces less stress on the coating than the PS system, allowing for thicker coatings while maintaining the integrity of the coating bond strength.¹⁸

Due these advantages, AWS was used as the surface treatment process for this project. Prior to this process it is vital that the substrate surface be cleaned or the coating will not have the desired properties, “Finally, it is important to keep roughening and spraying processes within a small interval of time (not more than a few hours). If the

interval is too long it will lead to surface oxidation and to a significant drop in sprayed coating bond strength."¹⁹

Arc Wire Spraying is shown in Figure (3)²⁰. Figure (3) is labeled to demonstrate how the AWS system operates. The atomizing gas, argon in this project, propels the molten metal forward. Two wires flow through the AWS system wire guides towards the nozzle at equal and opposite voltages.²¹ The arc occurs in the system as the two wires come in near contact with each other. This arc melts the wire, creating the molten particles that are sprayed forward by the atomizing gas.

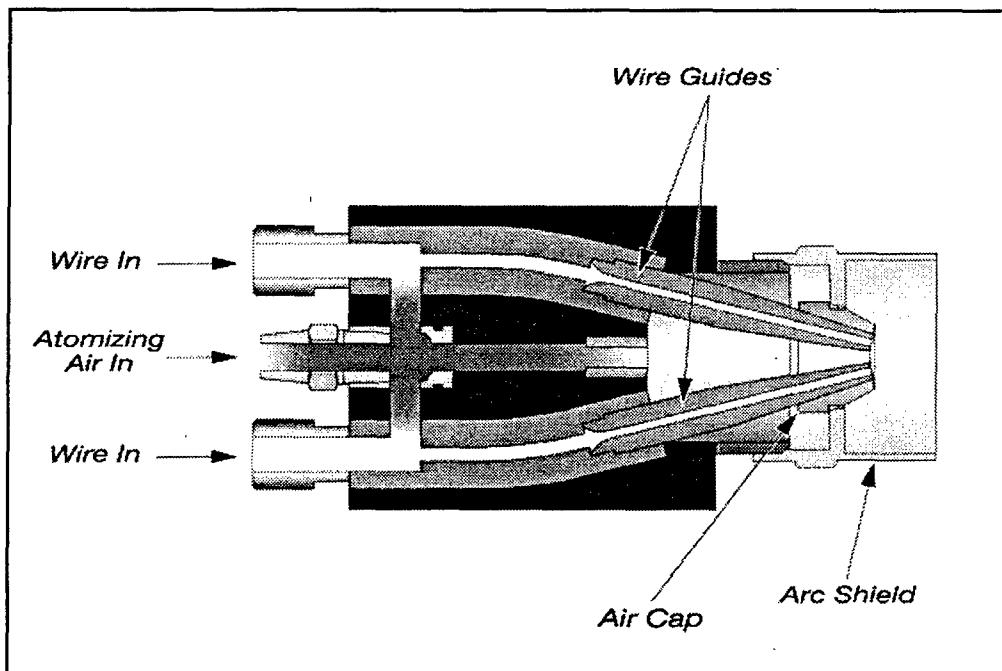


Figure 3 - Schematic of nozzle of Prox Air BP400 AWS system used by NSWCCD

Through experimentation and research in the arc spraying method it has been determined that any wire material used must be electrically conductive and range in size from 2 - 5 millimeters in diameter.²² The wires are atomized by the arc and the particles produced can reach velocities of up to 150 m/s. The arc may reach temperatures of up to 6100K by an arc current of 280A. A 200A current was used in this project. Finally, the arc voltage can range from 20 - 40 Volts.²³ By increasing the voltage, the droplet size can be increased. From the gas pressure, arc voltage, and arc current settings placed on the spray machine, the following average spray characteristics can be produced, Table (1).²⁴

Table 1 - Average spray characteristics produced by AWS

Deposition Rate	50 - 300 g/min
Spraying Distance	50 - 170mm
Atomizing gas pressure	0.2 - 0.7 Mpa

From these spray characteristics bond strengths varying from 10 - 30MPa can be produced and may be as high as 70MPa for NiAl coatings. The porosity of these coatings ranges from 10-20% and the coating thickness tends to range from 100 - 1500 μ m.²⁵

Through these processes, many different types of surfaces can be created. By using this data, a rough, porous surface was created. This rough, porous surface also produced a larger surface area for the paint to come in contact with and chemically adhere to. Chemical adhesion is the sharing of electrons between elements that allows their outer valence shells to become connected. By creating a rough, porous surface, the paint was able to flow into, and out of many pores, crevices, and voids. This creates a velcro type effect of adhesion, the

mechanical interlocking of two substances, which is called mechanical adhesion. With both the chemical and mechanical adhesion of the paint to the metal increased, the effects of the ICCP system on the bond strength of the propeller blade can be reduced.

EXPERIMENTAL PROCEDURE

PREPARATION OF NAB SPECIMENS

Nickel-Aluminum-Bronze (NAB) test specimens, 0.25 inches thick, were cut to a minimum dimension of five inches by two inches from large, 0.25 inches thick, NAB plates. These dimensions were essential because any specimen cut under the 2 X 5 inch dimensional requirements would not provide enough surface area to attach an adequate sized urethane peel strip. A total of 48 specimens were produced for flame spraying plus 6 specimens for control testing. Each specimen was then cleaned and prepared for thermal spraying by using grit blasting. The grit blasting used 140 grit alumina powder to remove any oxidation and dirt from the surface of each NAB test sample. The grit blasting was determined to be complete through visual inspection of the specimen's surface, and observing that all oxidation had been removed. Upon completion of the grit blasting process, each sample was rinsed with ethanol to remove any dirt, powder or organic residue left by the grit blasting process, and allowed to air dry.

THERMAL SPRAYING OF NAB SPECIMENS

A ProxAir BP400 Arc Wire Machine was used to spray a NAB coating onto the surfaces of the NAB test specimens. A high velocity tip was used as the nozzle on the arc wire machine due to its ability to focus the spray into a tight, concentrated pattern. The machine was run at its optimal operating settings of 28.1 V, 200 A, and 110 psi. Argon was used as the operating gas because it is an inert gas, and thus would not chemically react with the metal wires. NAB wires were used in order to create a surface of the same material as the substrate. The chemistry of the NAB wire and the NAB test specimen were almost identical as seen in Table (2).

Table 2 - Percent composition of NAB wire and test specimen

Element	NAB Wire	NAB Specimen
Al	9.9	8.91
Co	<0.01	<0.01
Cu	80.36	81.47
Fe	4.21	4.12
Mn	0.78	0.92
Ni	4.74	4.56
Pb	<0.01	<0.01
Si	<0.01	<0.01

These settings allow for the most efficient arc to be created, the most effective wire feed rate to be used, and the best gas pressure for propelling the molten particles forward²⁶. If the settings were placed above this, sputtering would occur, which would create a bad spray pattern. If the settings were placed below these values, the wires would not melt as efficiently, and solid sputtering could occur. The parameter varied in the spray process was the distance of the spray nozzle tip from the plate surface. The spray distance was varied in

six inch intervals out to two feet, measured from the test sample's surface. Twelve plates were sprayed at six inches, twelve at 12 inches, twelve at 18 inches, and twelve at 24 inches, for a total of 48 test samples.

Prior to spraying the NAB samples, a specific spray pattern was developed, and was held constant throughout the experiment. The spray pattern consisted of setting three plates in a row equidistant from the spray gun. The pattern began by moving the nozzle from left to right, then right to left while moving the nozzle from the top to the bottom of the three plates. Once the spray reached the bottom of the plates, the pattern changed to a vertical pattern. The nozzle was then moved from the bottom to the top of the test sample. The vertical pattern began on the left side of the test samples and moved to the right side. The entire sequence was repeated until a thermal coating of 0.015 in +/- 0.003 in was placed onto the NAB plate. The coating thickness was determined by using a handheld micrometer. One cycle of the spray pattern is shown in Figure (4).

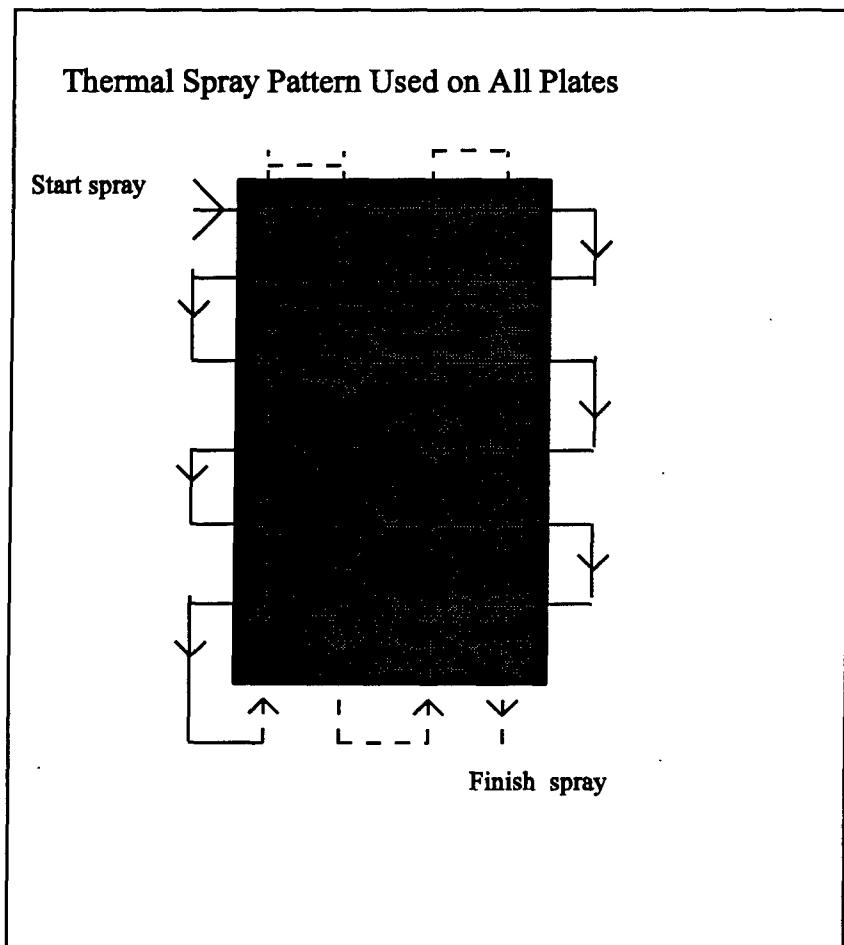


Figure 4 - One cycle of thermal spray pattern used in the Arc Wire spraying process.

OPTICAL MICROSCOPY

One sample of each spray distance was mounted, cut, polished, and viewed in cross-section under a Nikon optical microscope at magnifications ranging from 10X to 20X. Climex Vision software was used to analyze and classify the porosity and oxidation of the surface morphology created at each spray distance. A gray scale analysis program was used to determine the percent area of porosity and oxidation on the cross-section of each surface. The porosity, black colors on the surface, were shaded blue, and the grey colored oxidation was colored red. The program then performed an area analysis of the percent of "blue" porosity and "red" oxidation covering the observable surface. An image analysis box was entered into the program with preset dimensions to ensure that only the porosity and oxidation of the thermally sprayed coating was evaluated. Each of the four spray distances were evaluated using this procedure to characterize their surface morphology.

PLATE DIVISION

A total of 54 plates were tested and evaluated. Twelve plates were sprayed at each distance under the previously mentioned spray conditions of 28.1V, 200A, 110 psi, and the use of a high velocity nozzle. This produced a total of 48 NAB coated plates, or four sets of 12 plates for testing at specified time intervals. Each set of twelve plates were subdivided into four subsets of three plates. These four subsets of three plates corresponded to the four spray distances of six, 12, 18, and 24 inches from the plate surface. The four sets of twelve plates represented the testing cycle of zero, 25, 50, and 75 days of environmental exposure as seen in Figure (5).

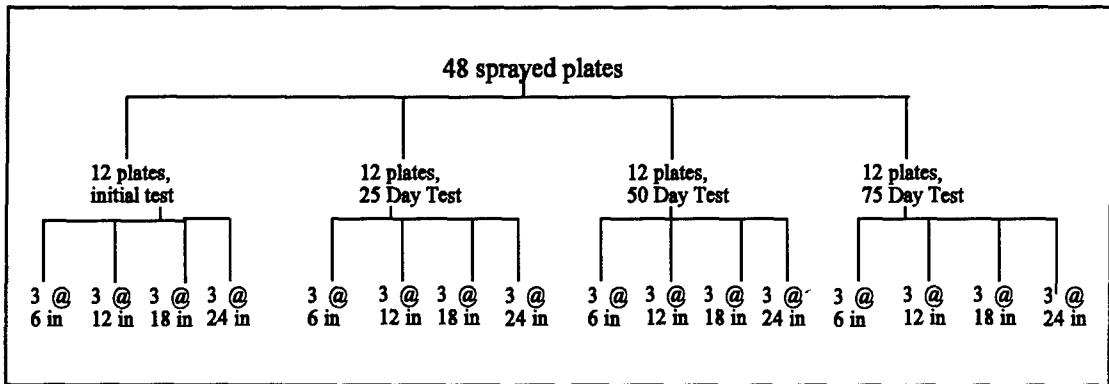


Figure 5 - Flow chart of test specimen organization.

The remaining six plates were control samples, and were not thermally sprayed.

The control plates were divided into two sets of three plates. This division corresponded to the testing cycle of zero and 25 days. The break down of the control test plates can be seen in Figure (6)

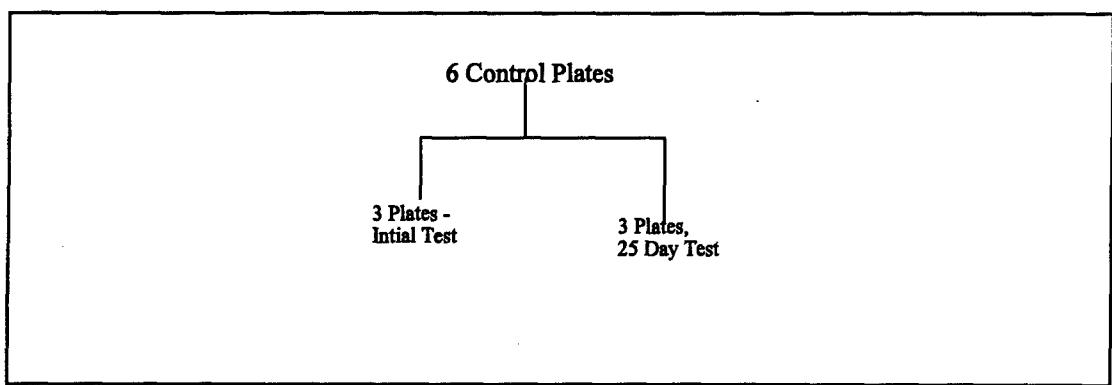


Figure 6 - Flow chart of control specimen organization.

PLATE PAINTING

Both the test and control samples were painted using the same paint and application technique, since the NAB on a SEAWOLF propeller blade is painted in order to reduce corrosion rate of the propeller blade. Additionally, the paint acts as the adhering agent between the urethane and the substrate, since the urethane adheres poorly when applied directly onto the NAB substrate. After completion of the thermal spray process, the test specimens were painted. The six control samples were painted after completion of the grit blasting process.

The painting process began with an application of a primer coat of 2842-1109 series paint. The surface of the sample was covered with this paint and allowed to cure for 24 hours. A finishing coat of 2842-1110 series paint was then applied to the sample's surface and allowed to cure for an additional 24 hours. The only difference between the two paints was that the -1109 was an orange colored paint and -1110 was a black paint. The chemical properties of the paints were identical, except for the chemicals which produced their colored appearance. This was done to allow the applicator to visually confirm that two coats had been placed on the test specimen. Once the paint had finished curing, the painted surface was sanded using standard 80 grit sand paper to remove any surface oxidation and dirt that accumulated on the surface of the paint. The painting and sanding process results can be seen in Figures (7) and (8).

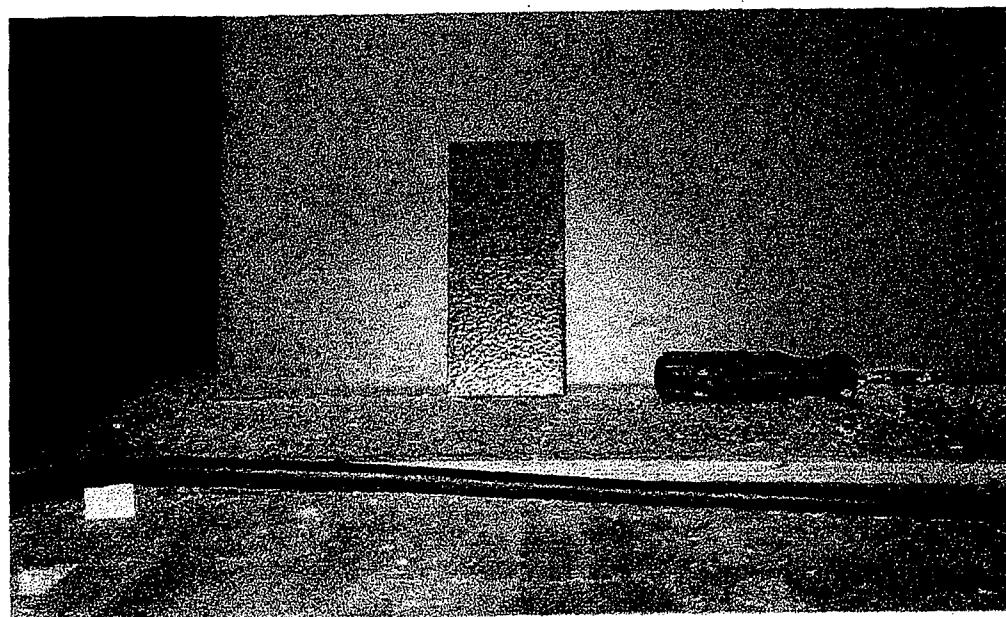


Figure 7 - Final view of 2842 series painted test specimen after application of two coats of paint.

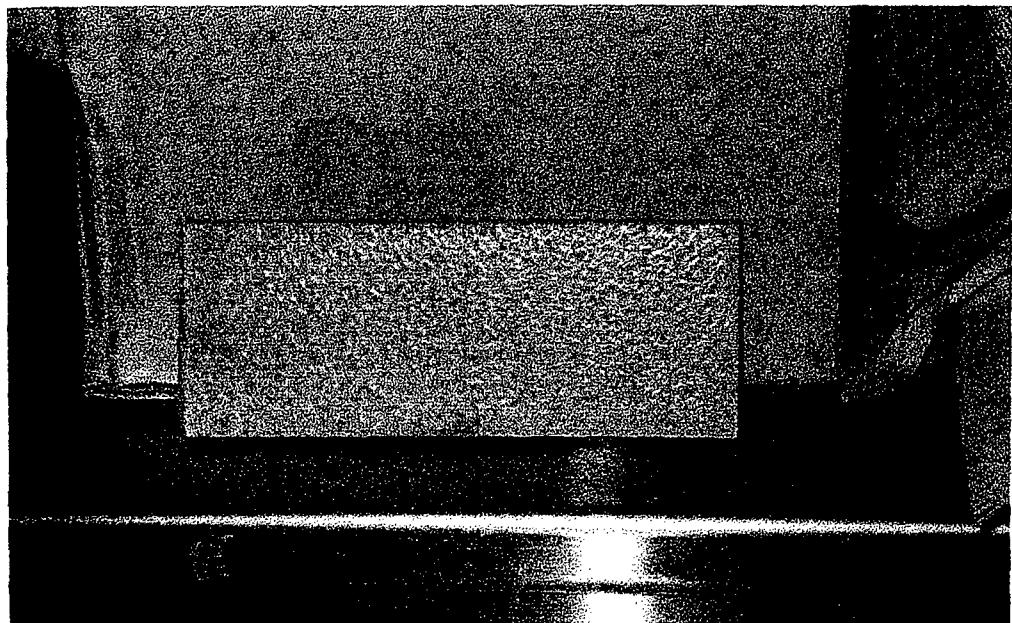


Figure 8 - View of a sanded test specimen, notice the lack of a surface sheen which indicates that all dirt and oxidation had been removed.

URETHANE APPLICATION

After completion of the painting process, the urethane coating was applied to the test specimen. Prior to pouring the urethane, the test specimens were cleaned with MEK, methyl ethyl ketone, and allowed to air dry. A three inch by one and a half inch piece of duct tape was then placed on one end of the test specimen. The duct tape prevented the urethane from adhering to the plate over that one inch area. This loose, 1.5 inch section of urethane, was later fixed in the peel test clamps so that the 90-degree peel test could be performed. The coating of urethane was applied by hand pouring liquid urethane into a 0.5 inch thick, 1 inch wide, and 10 inch long mold placed on top of the test specimen. A large machined plate was used that contained six of these molds in order to increase the number of samples that could be cast at one time. The urethane was prepared by mixing four parts Versalink P-1000 with one part Isonate 2143L. Prior to mixing these two substances, they were individually degassed in a vacuum for five minutes to remove any excess gas that had accumulated in the chemicals. After degassing, the chemicals were mixed, and then the combination was again degassed for three minutes. This short degassing time was due to the relatively short curing time of the urethane, which was between five and six minutes. After degassing, the urethane was poured into the mold to a thickness of 0.25 in. Once all the specimens had been coated, they were allowed to cure for one week prior to removal from the mold. The mold used, and a poured casting are shown in Figure (9).

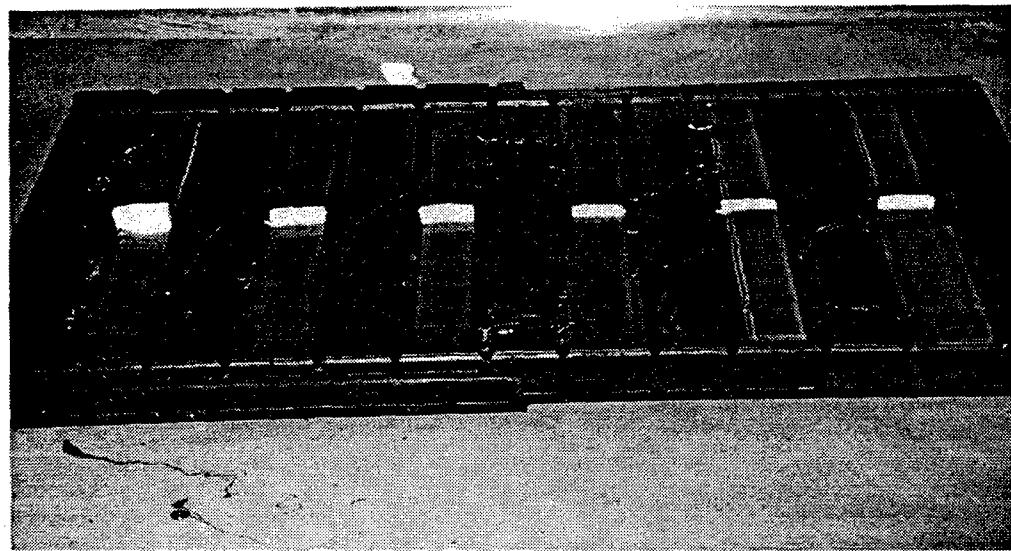


Figure 9 - Urethane poured and curing on top of test specimens. Twelve test samples are placed under this mold for coating in urethane.

SEAWATER / CATHODIC PROTECTION EXPOSURES:

Three coated plates from each spray distance were placed into a salt water tank under cathodic protection, as seen previously in the test specimen organization shown in Figure (6). Twelve tanks were present and were subdivided into groups of four tanks. Each group of four represented an exposure time for the test specimens. Each tank within that subset corresponded directly to a specific thermal spray distance. The organization of the salt water tanks is shown in Figure (10).

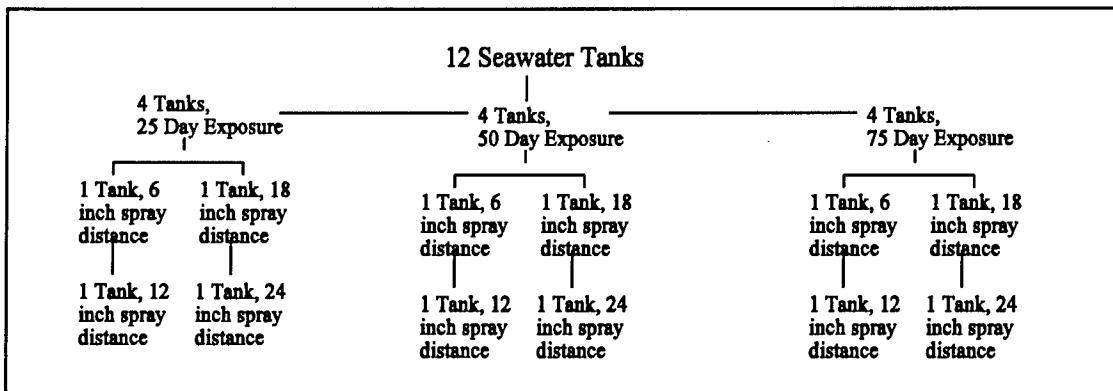


Figure 10- Flow chart of Seawater tank organization.

The seawater in each tank was created by placing 3.5g of sea salt, as per ASTM D1141-52, into the tank for every 100g of distilled water placed into the tank. Distilled water was continually added to each tank throughout the exposure time period in order to maintain the proper salinity, and overcome the effects of evaporation. This was done approximately every five days throughout the entire 75 day test period. The composition of the sea salt is given in Table (3).

Table 3 - composition of ASTM D1141-52 Sea-Salt.

NaCl	58.490
MgCl ₂ - 6H ₂ O	26.460
Na ₂ SO ₄	9.750
CaCl ₂	2.765
KCl	1.645
NaHCO ₃	0.477
KBr	0.238
H ₃ BO ₃	0.071
SrCl ₂ - 6H ₂ O	0.0095
NaF	0.007

*Sea-Salt Contains elements found in natural sea salt in quantities greater than 0.004%

Cathodic protection was accomplished in each tank by electrically connecting a zinc anode to all three of the NAB plates submerged in the salt water environment. The plates were electrically connected by 8 gauge electrical wire, which was then connected to a 1 - 5 $k\Omega$ variable resistor in-between the zinc anode and the three plates. The electrical wire was connected to the NAB plates, and the zinc anode, by 60/40 tin-lead solder. The zinc anode was then connected to the resistor to complete the circuit. Once the circuit was completed, the potential of the NAB plates were measured relative to a saturated calomel reference electrode, SCE, using a voltmeter. The resistor was then adjusted to bring the potential of the NAB test plates to a reference potential of -0.850V vs. SCE, which is approximately equal to the typical cathodic protection level of metallic components on U.S. Navy vessels. The potential for each of the 12 salt water tanks was measured and adjusted on a daily basis throughout the required exposure time. A typical salt water tank with a zinc anode electrically connected to three test NAB plates can be seen in Figure (11).

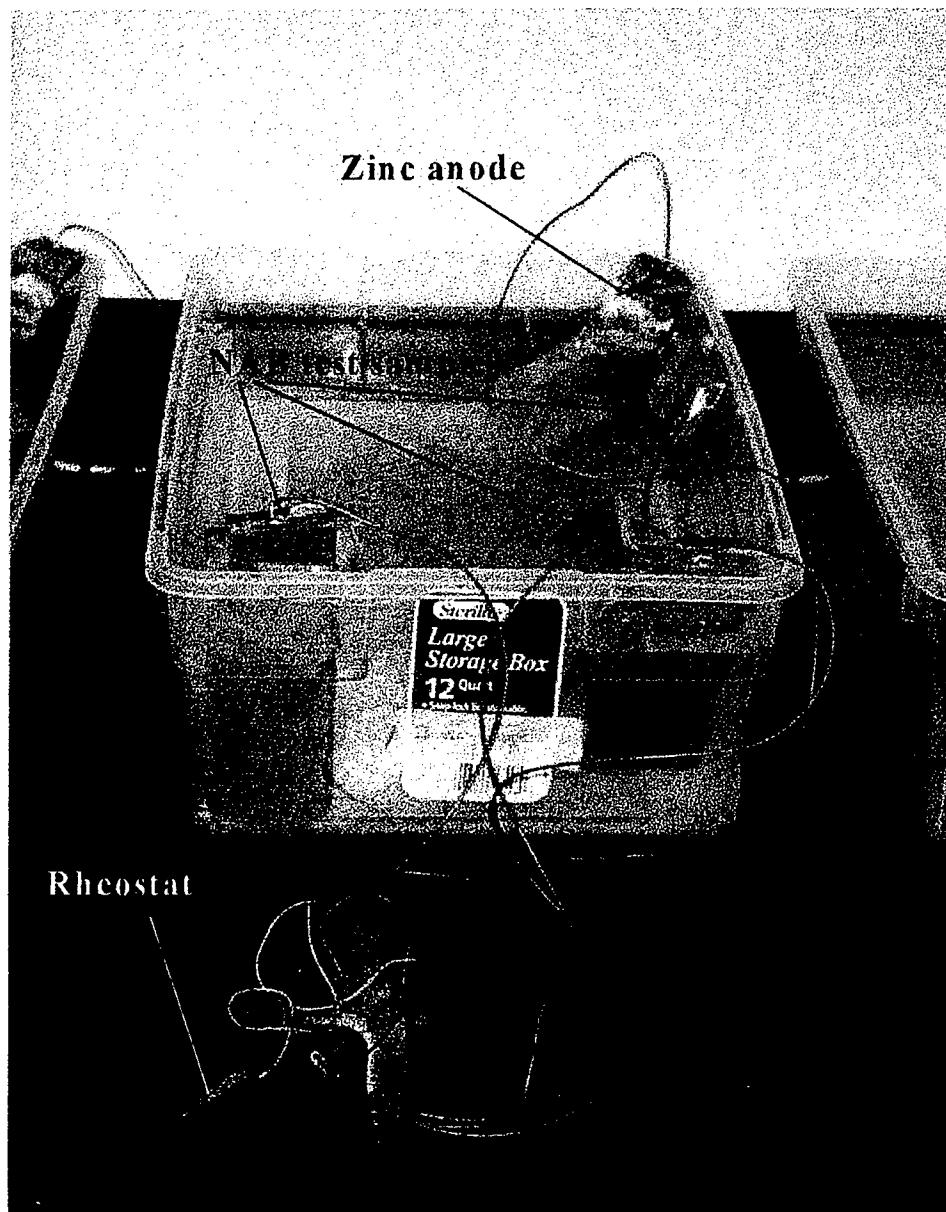


Figure 11 - Typical exposure tank of salt water, zinc anode, NAB test plates, and rheostat.

NINETY-DEGREE PEEL TEST:

A 90-degree Peel Test was used to examine the bond strength of the specimens. A SATEC tensile test machine was used with a 2000 lb. load cell rising at a rate of 2 in. / min. The test was run by clamping the front end of the peel strip in to a pneumatic grip pressurized to 100 psi. The test configuration can be seen in Figure (12).

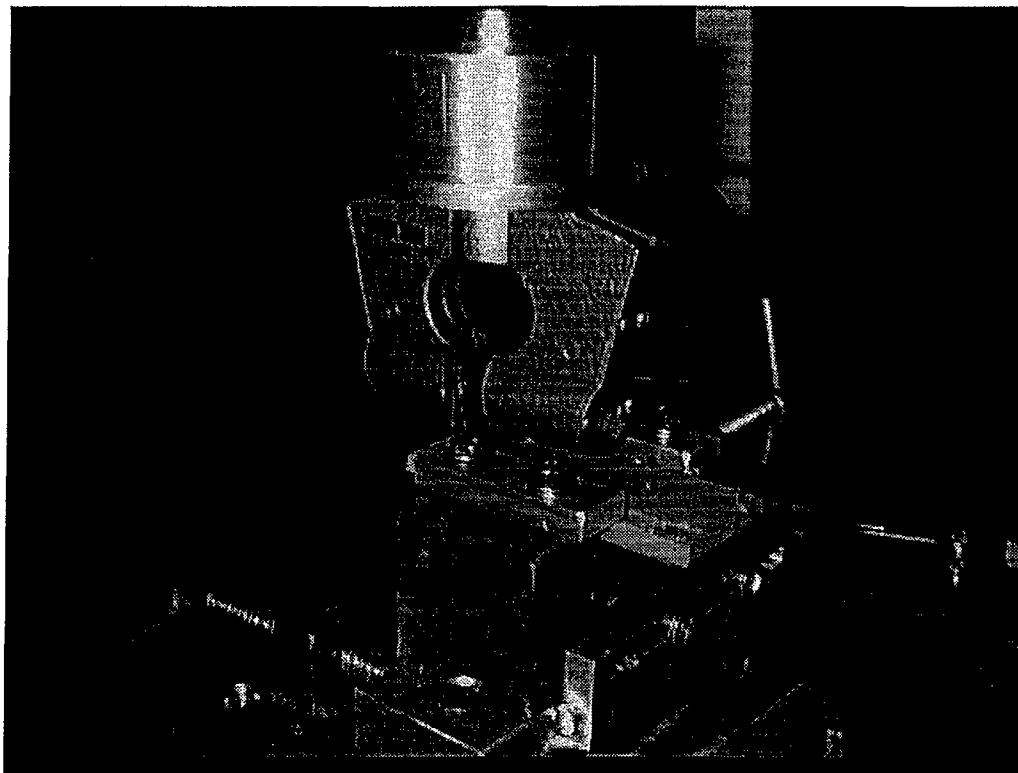


Figure 12 - One inch free end of urethane peel strip clamped into a pneumatic grip under 100psi pressure.

The SATEC imposed a displacement of the urethane by pulling up on it at a constant displacement rate, and measuring the resulting load. The machine measured the load required to pull the strip off the plate by using this process. As the urethane separated from the plate, the plate was slid forward in order to maintain a 90-degree angle between the urethane peel strip and the test plate as shown in Figure (13).

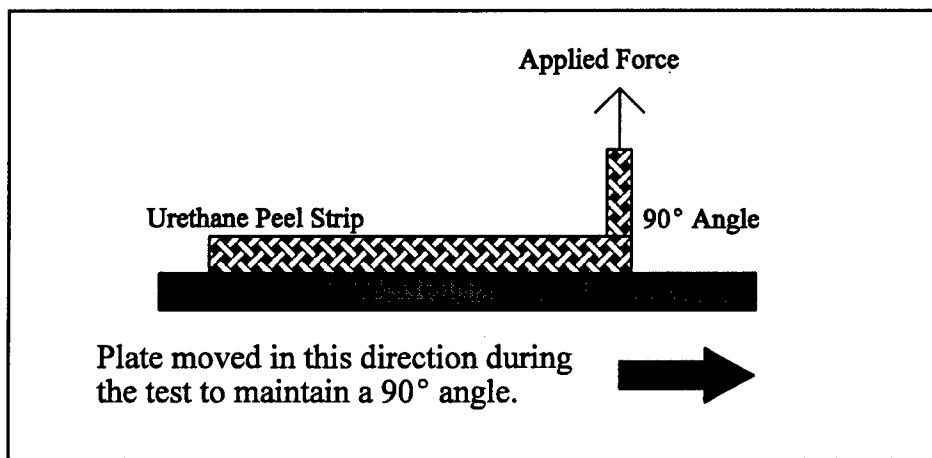


Figure 13 - Schematic view of a 90-degree peel test.

After the test was completed, a plot of the load versus the upward displacement was created. This plot allowed for the determination of the bond strength of the overall system of urethane, paint, thermal spray coating, and NAB substrate. In order to obtain an accurate bond strength, three values from the plot were recorded. An initial elastic region occurred on the plot which was due to the urethane properties. The urethane was elastic and would stretch until the bond interface failed. The initial measured load corresponded to the deformation of the urethane while the later measurements corresponded to the load required to break the bond between the urethane and paint or the paint and NAB. The load held by the system after the elastic region was recorded as the maximum bond

strength. The smallest load held by the system after the elastic region on the plot was recorded as the minimum bond strength. Finally, an approximation of the overall bond strength was obtained by drawing a straight line through the plot that visually represented the average bond strength. This final measurement was based on visual interpretation of the plot, the peel surface, and the mode of failure. The peel surface indicated the mode of failure by the type of material present on the peel strip, and left on the plate surface. The thermal spray coating failed if the paint was entirely removed from the test specimen during the peel test, adhering to the urethane peel strip. If the paint remained entirely adhered to the test specimen during the peel test, the mode of failure was the paint-urethane interface. If failure occurred within the thermal sprayed coating, then that sample failed to meet the required bond strength of the system. Samples of various plots are shown in Figures (14) and (15). Various peaks and valleys can be seen in the Load vs. Distance plot in Figure (15). These variations were likely caused by the varying amount of cathodic protection present across the test specimen. The cathodic protection system did not protect the entire plate equally, therefore various parts of the sample had better adhesion characteristics than other parts. The valleys also represent either a scoring location, a place where the urethane was cut at the paint-urethane interface to balance the peel strip, or a failure of the thermally sprayed coating. These valleys are common in peel tests, specifically when testing samples that were previously exposed to cathodic protection.

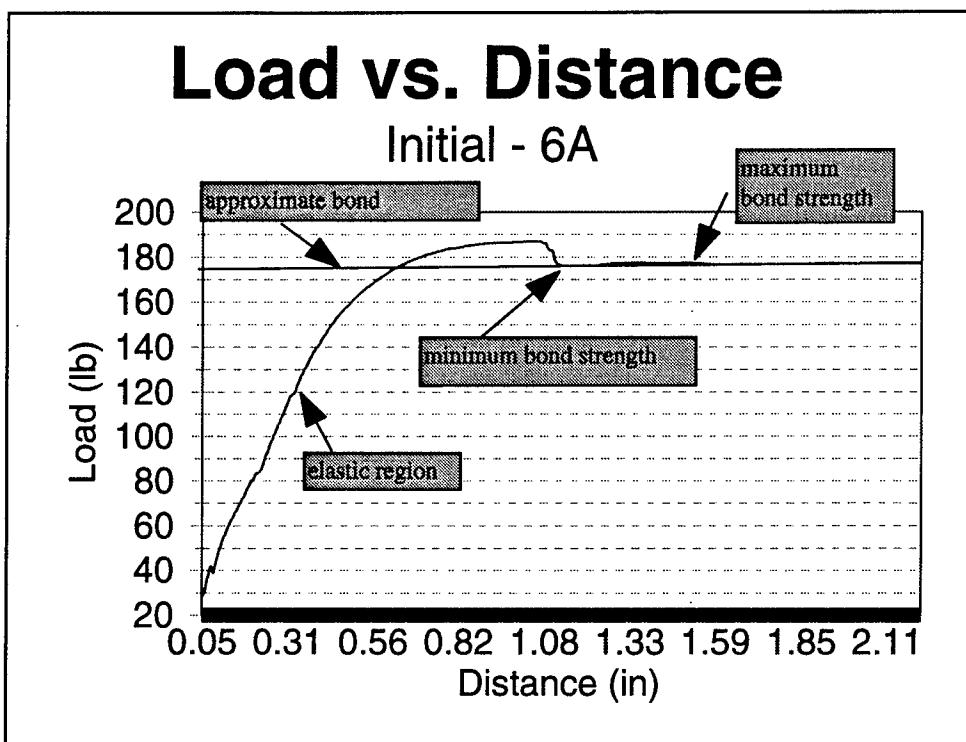


Figure 14 - Sample of Peel Test Data interpretation.

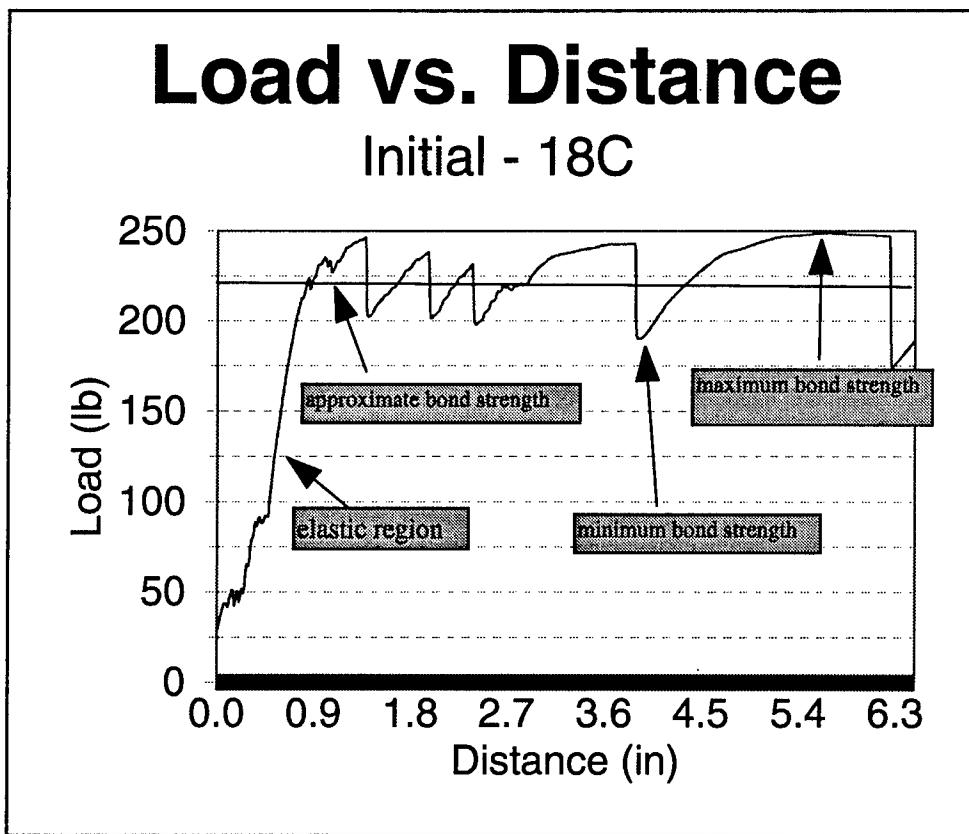


Figure 15 - Sample of Peel Test Data interpretation.

SEM ANALYSIS AND X-RAY MICRO-ANALYSIS

The peel surfaces were visually examined to determine the location of the break, what material failed, and the mode of failure. In order to determine what materials separated from the plate during the peel test, a section of the peel strip was placed in the SEM, and an x-ray micro-analysis using a KEVEX image analysis program was performed. The x-ray analysis was used to determine the elements present on the peel strip, which would indicate whether or not the thermally sprayed coating failed, the paint - urethane interface failed, or the paint - thermally sprayed coating interface failed. The x-ray analysis was performed with an SEM accelerating voltage of 20 KeV. The samples were coated with a thin gold-palladium coating by sputtering for two minutes prior to placement in the SEM. When viewing the spectrum created by the x-ray analysis, spikes should be seen indicating silicon, chlorine, sodium, potassium, calcium, copper, aluminum, and nickel. These elements correspond to the sea salt, paint, and nickel-aluminum-bronze. X-ray micro-analysis worked by sending electrons into the test peel strip in the SEM, causing inner shell electron vacancies. The electrons in each element would then shift down to a lower energy level within the atom structure. When this occurred, the atom would release energy, sometimes in the form of x-rays. Each element emitted x-rays at specific wavelengths which corresponded to that element. These x-rays were detected by the KEVEX instrumentation and plotted in a spectrum.

RESULTS AND DISCUSSION

THERMAL SPRAY SURFACE EVALUATION

The properties of the thermally sprayed coating varied significantly as the spray distance was increased, specifically the porosity and oxidation within the sprayed coating itself. In order to create a mechanical bond with the paint, a highly porous surface was desired. Through consultation and literature review, it was determined that spray distance had the greatest effect on the porosity characteristics of a thermal sprayed surface. Additionally, as will be presented, it was determined that the spray distance has a profound effect on the strength of the thermal spray coating. As the coating was applied closer to the plate, the bond strength between the coating and substrate, and between the thermal spray layers, greatly increased. As the spray distance from the specimen increased, the bond strengths between the coating and substrate, and coating layers, decreased to the point that the coating could not support any loading.²⁷ Through experimentation and consultation, four spray distances at equal intervals were chosen for study. The four spray distances were; six inches, 12 inches, 18 inches, and 24 inches from the spray nozzle to plate surface. Porosity is defined as the cavities and voids present on a surface that allow for another material to freely flow into, and out of, the specific area. The porosity of the surface can be seen in Figure (16) by the black color as labeled. Oxidation is caused by a chemical reaction that occurs between the air and the hot NAB spray during spraying, and can be seen in Figure (16) by the greyish color indicated on the picture.²⁸ The oxidation lines move linearly in a horizontal direction, indicating that the thermal spray coating is building up layer by layer. The swirling gray lines indicate a mixing, which means that one layer is being

remelted as a new layer hits the surface. This mixing causes lower porosity because the remelted metal fills in the pores that were just created.

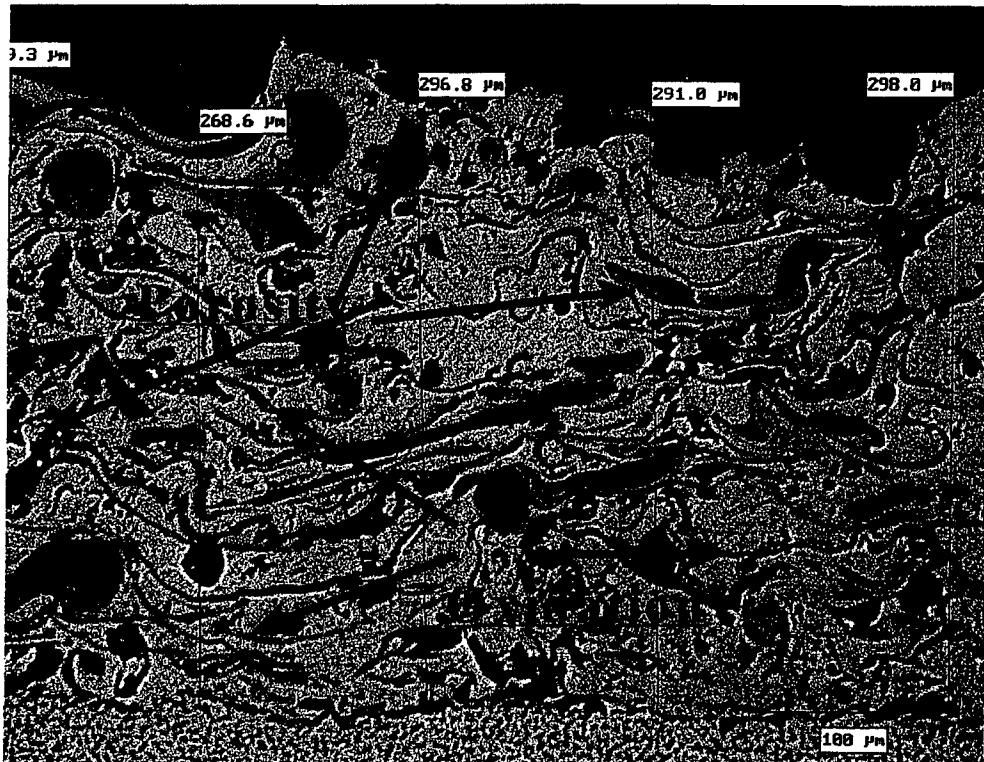


Figure 16 - View of 12 inch thermal spray distance showing oxidation (red lines) and oxidation, (blue lines).

From these definitions, porosity and oxidation measurements for the individual spray distances were determined and are presented in Table (4).

Table 4 - Average porosity and oxidation for various AWS spray distances.

Spray Distance (in)	Average Porosity (%Area)	Average Oxidation (% Area)
6	10.78	13.63
12	13.75	12.78
18	15.47	15.57
24	17.19	15.98

As Table (4) reveals, porosity increases with spray distance. The increased porosity can be seen in Figures (17) to (20), which represent a typical cross-section of a thermally sprayed plate from each distance. High porosity was desired, because the greater the porosity, the stronger the mechanical bond between the paint and substrate. Although the porosity increased with spray distance, so did the percent area of oxidation on the thermal coating as shown in Table (4). This oxidation can prevent a strong bond from forming between the thermal sprayed coating layers as they pile up on top of each other during the coating process. The effect of the strong mechanical bond, created with the greater porosity, can be counteracted by the weakened interlayer bond within the thermal sprayed coating caused by the increased level of oxidation. If this interlayer bond becomes weaker than the mechanical and chemical bonding between the paint and substrate, the applied coating becomes useless. Due to these conditions, it becomes necessary to balance out the positive effects of increased porosity, with the detrimental effects of increased oxidation levels.

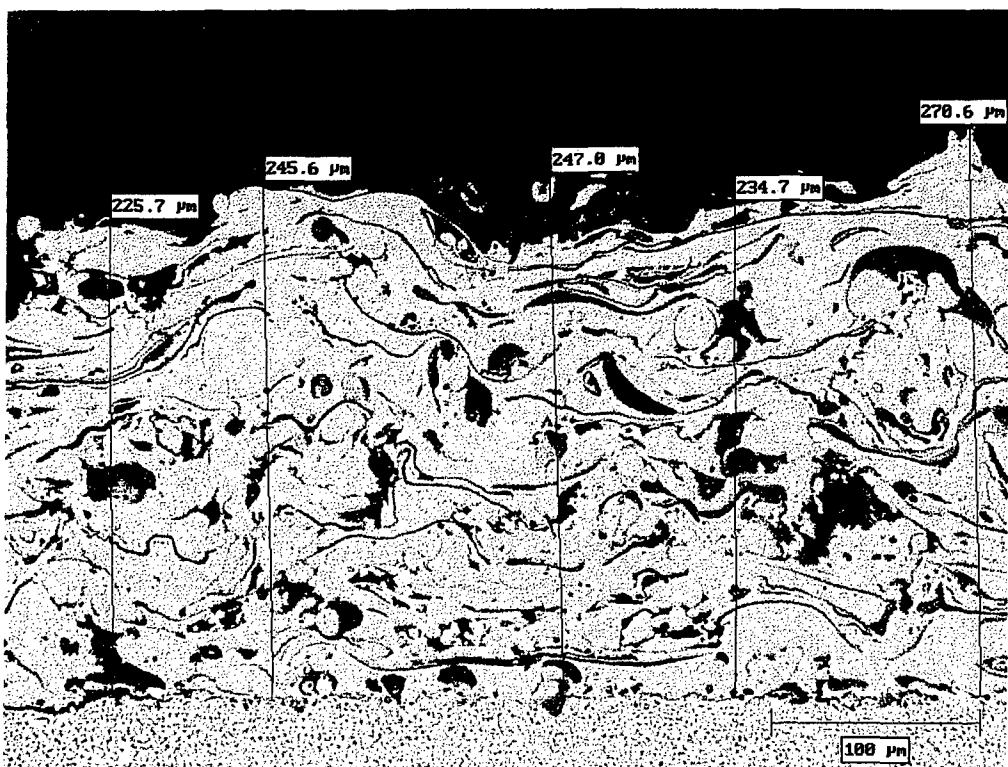


Figure 17 - 6 inch spray distance, 20X Magnification

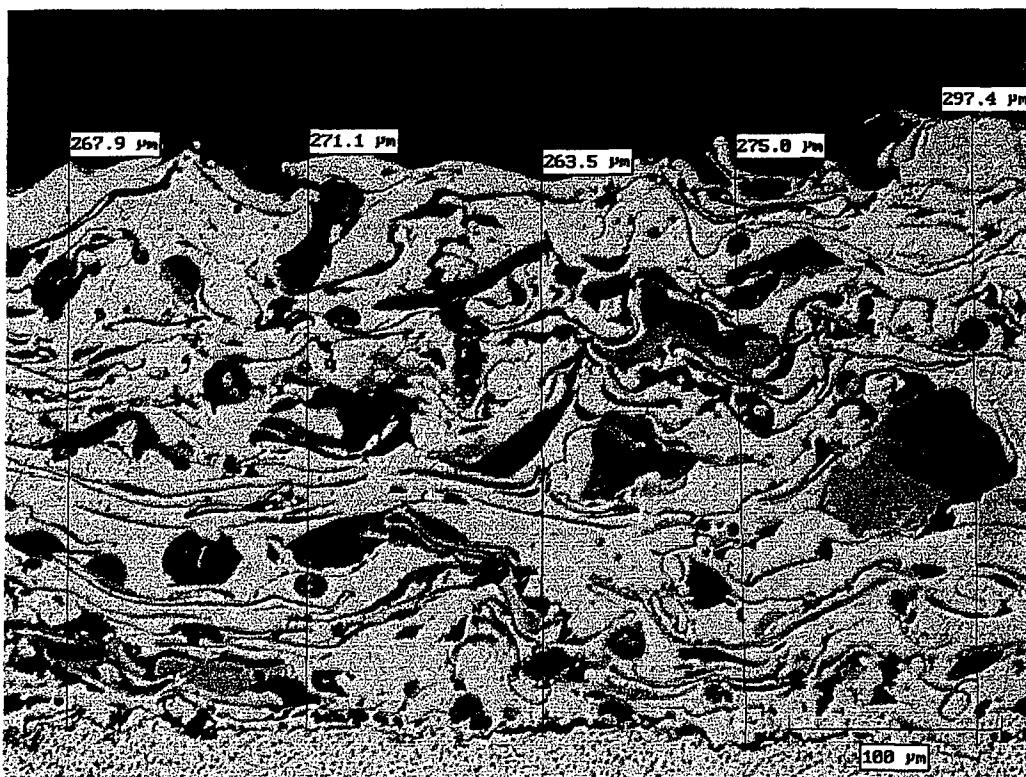


Figure 18 - 12 inch spray distance, 20X Magnification

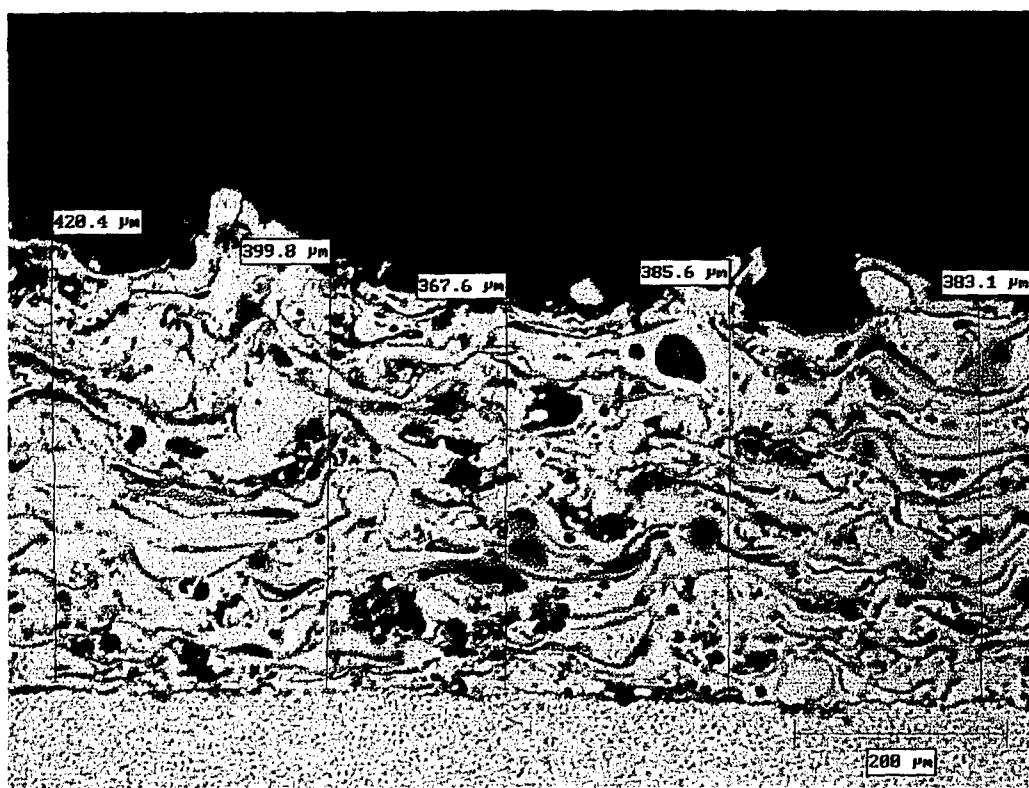


Figure 19 - 18 inch spray distance, 10X Magnification

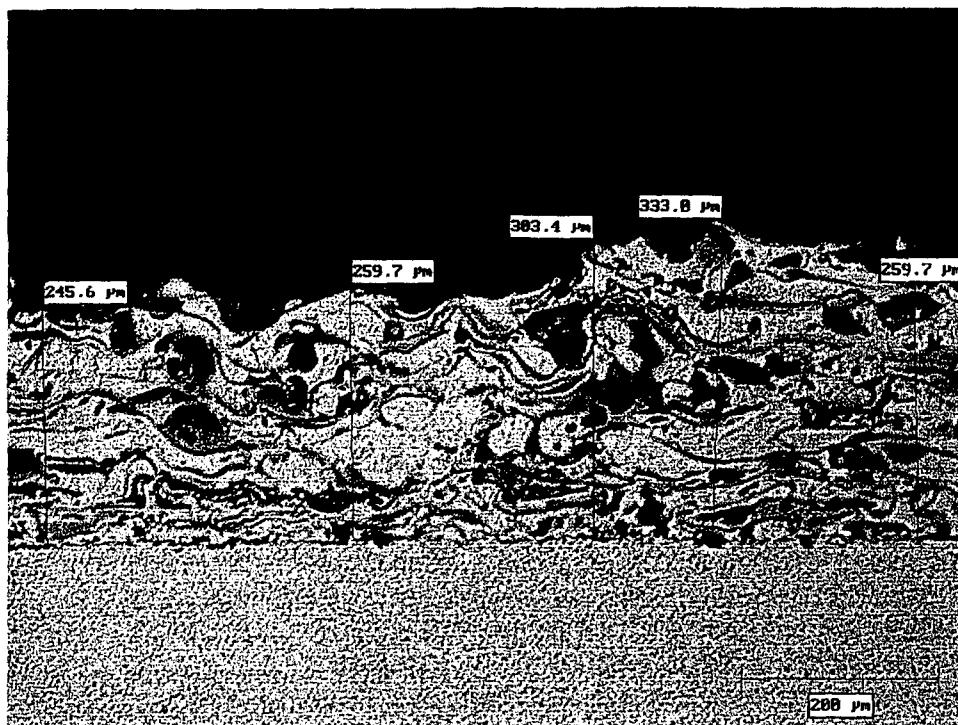


Figure 20 - 24 inch spray distance, 10X Magnification

CATHODIC PROTECTION TESTS

As described previously, values of the NAB potentials for each saltwater tank were recorded on a daily basis. After the test specimens were removed from the tanks, an average value and standard deviation were determined for the NAB potential from each tank. The results for each tanks, and a sample data plot, are given below in Table (5) and Figure (21).

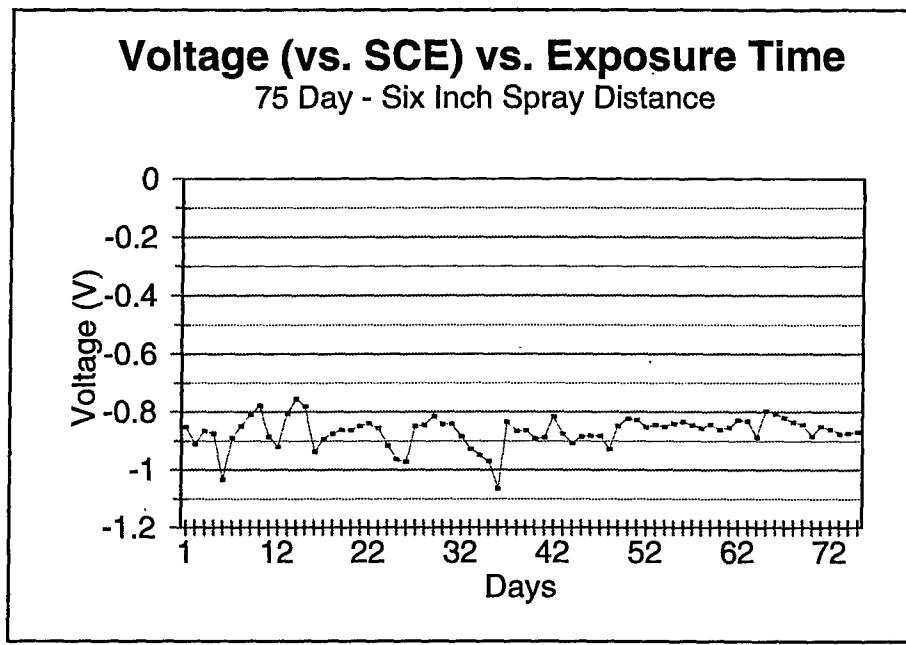


Figure 21 - Sample Plot of NAB Potential over time for the 6 inch spray distance and a time period of 75 Days

Table 5 - Average potentials for test specimens after specified exposure times

Time Period (Days)	Spray Distance (in)	Average Potential (Volts vs. SCE)	Standard Deviation (Volts vs. SCE)
25	6	-0.862	0.062
25	12	-0.854	0.094
25	18	-0.876	0.068
25	24	-0.858	0.151
50	6	-0.882	0.132
50	12	-0.871	0.085
50	18	-0.861	0.089
50	24	-0.852	0.110
75	6	-0.867	0.060
75	12	-0.873	0.127
75	18	-0.873	0.071
75	24	-0.884	0.090

The average values indicate that all exposed plates were maintained at potentials within reasonable variances of -0.850V vs. SCE as desired. The corrosion rate and hydroxyl ion production were, therefore, maintained at a realistic level on the test specimens.

ADHESION STRENGTH TESTS

The 90°peel test was used to evaluate the bond strength of the paint, urethane, NAB system. The 90°peel test evaluated the bond strength of the NAB sample in terms of pounds per linear inch of peel strip width as shown in Equation (2).

Force to cause debonding (lbs) / width of urethane peel strip (in) (**Equation 2**)

In this experiment, a one inch wide peel strip was used so that the load readings from the SATEC testing machine would correspond directly to the bond strength of the NAB test specimen. The peel test was performed on each plate, and a plot of the load versus the distance was produced. Graphical representations of the results can be seen in Figures (22) to (27). Data for each test specimen, at each spray distance, can be seen in Tables (6) to (10).

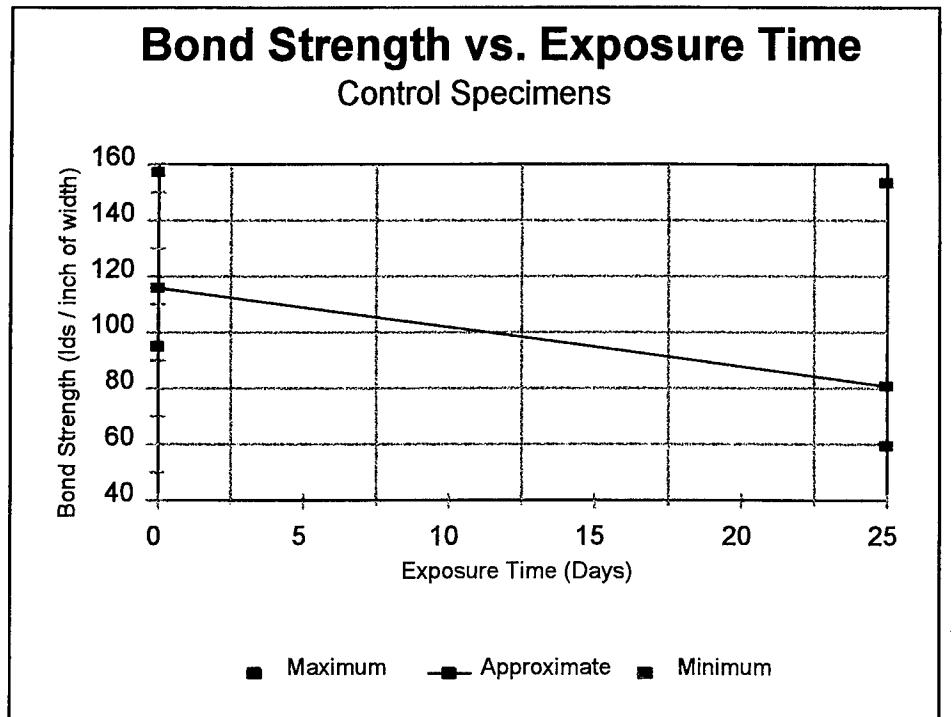


Figure 22 - Plot of bond strength vs. exposure time for non-thermal sprayed control specimens.

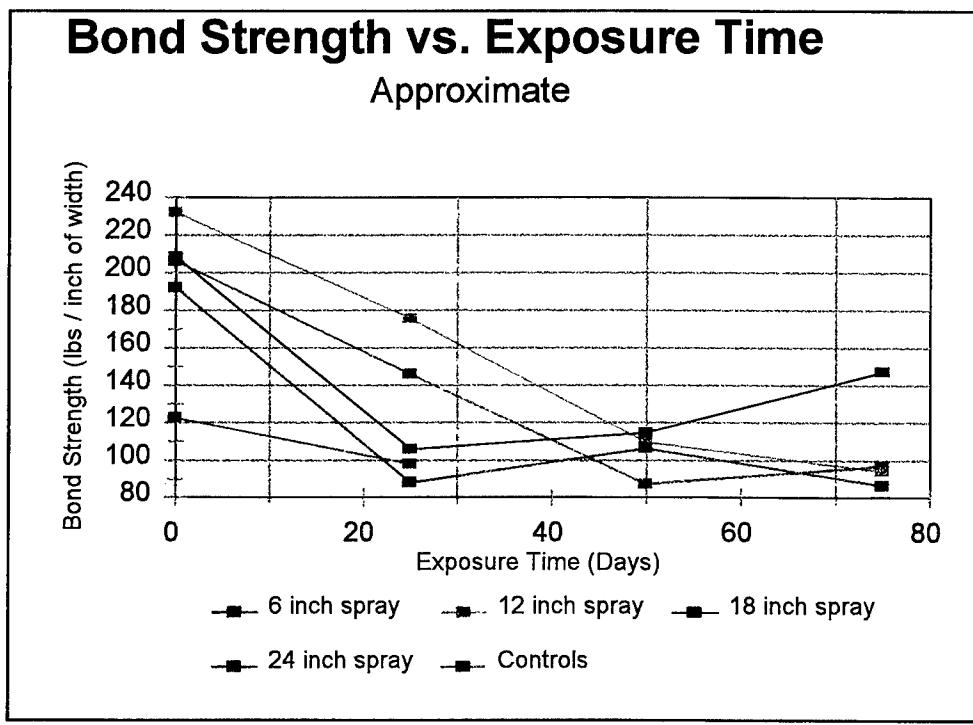


Figure 23 - Plot of the average approximate bond strengths vs. exposure time for each spray distance and control specimens.

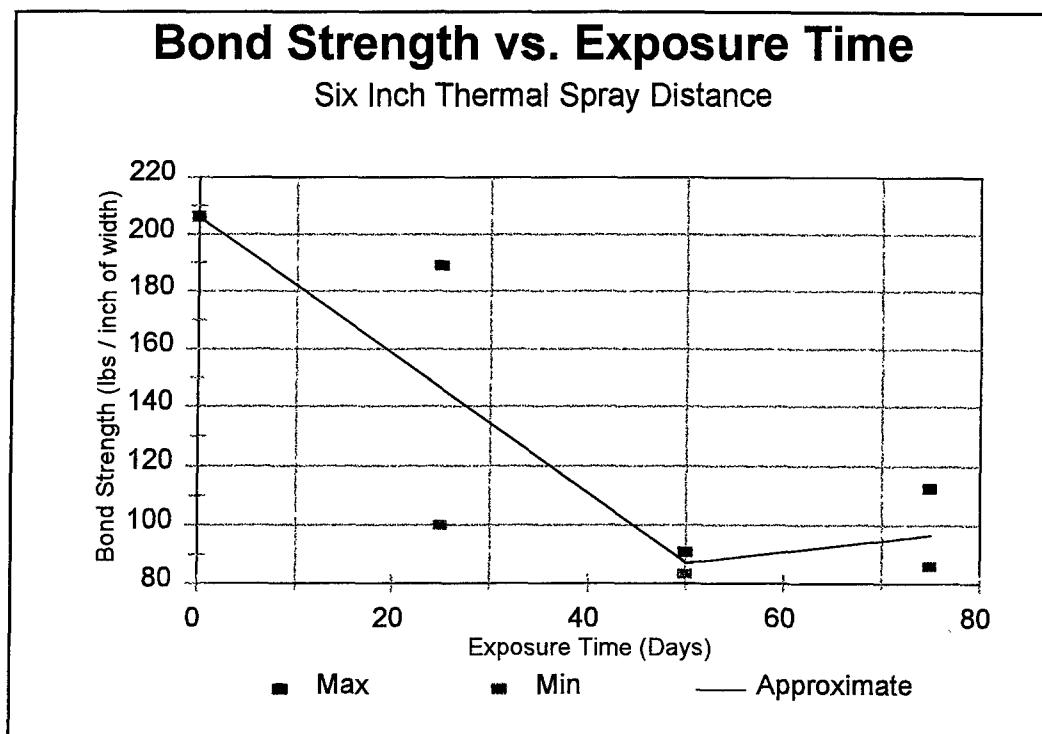


Figure 24 - Plot of bond strength for six inch spray distance at preset exposure times.

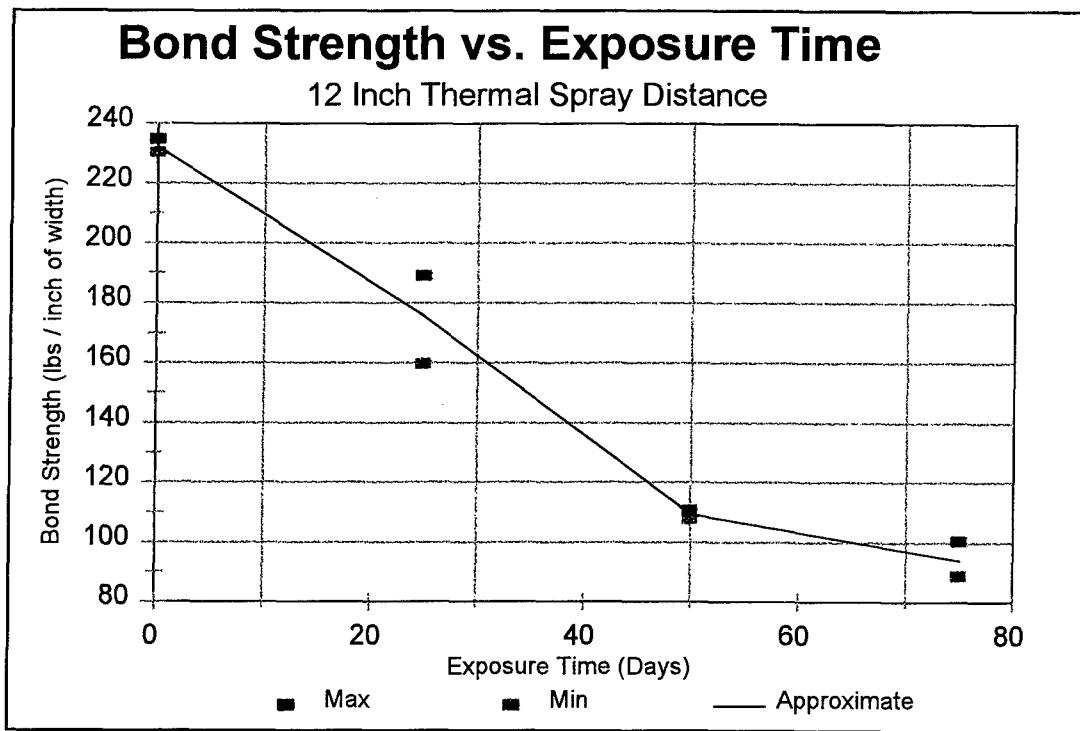


Figure 25 - Plot of bond strength for twelve inch spray distance at preset exposure times.

Bond Strength vs. Exposure Time

18 Inch Thermal Spray Distance

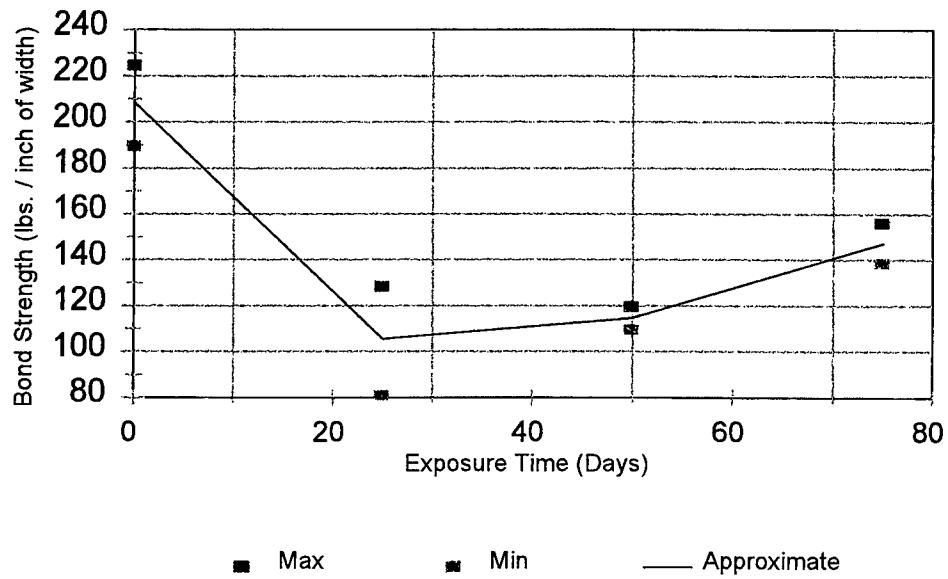


Figure 26 - Plot of bond strength for 18 inch spray distance at preset exposure times.

Bond Strength vs. Exposure Time

24 Inch Thermal Spray Distance

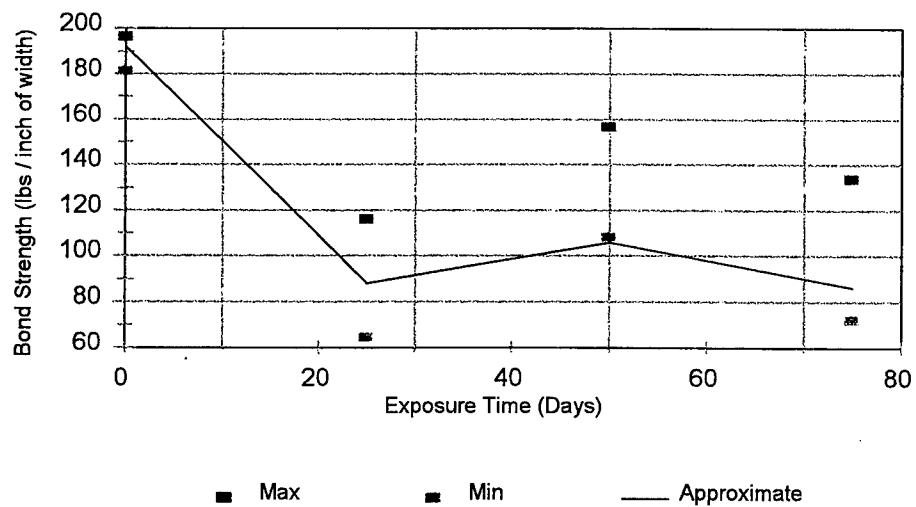


Figure 27 - Plot of bond strength for 24 inch spray distance at preset exposure times.

Six Inch Spray

Distance

Test Period Days	Test Plate	High Bond Strength lb. / inch of width	Low Bond Strength lb. / inch of width	Approximate Bond Strength lb. / inch of width
0	a	177.49	177.49	177.49
0	b	205.49	203.87	204
0	c	236.7	236.7	236.7
25	a	175	78	140
25	b	188	55	110
25	c	204	167	188
50	a	90	83	87
50	b	82	77	79
50	c	100	90	95
75	a	105	90	97
75	b	137	96	115
75	c	95	72	78

Table 6 - 90-degree peel test results for six inch spray distance.

12 Inch Spray

Distance

Test Period Days	Test Plate	High Bond Strength lb. / inch of width	Low Bond Strength lb. / inch of width	Approximate Bond Strength lb. / inch of width
0	a	230	230	230
0	b	240	233.8	236
0	c	234	227	230
25	a	198	174	184.6
25	b	164	130	150
25	c	205	175	192
50	a	97	95	96
50	b	96	90	93
50	c	139	138	139
75	a	95	83	90
75	b	110	105	108
75	c	96	78	84

Table 7 - 90-degree peel test results for twelve inch spray distance.

18 Inch Spray

Distance

Test Period Days	Test Plate	High Bond Strength	Low Bond Strength	Approximate Bond Strength
		lb. / inch of width	lb. / inch of width	lb. / inch of width
0	a	213	213	213
0	b	210	160	192
0	c	250	195	220
25	a	100	70	84
25	b	140	100	125
25	c	144	72	108
50	a	135	125	130
50	b	118	105	112
50	c	105	98	102
75	a	166	157	160
75	b	196	180	186
75	c	106	78	96

Table 8 - 90-degree peel test results for eighteen inch spray distance.

24 Inch Spray

Distance

Test Period Days	Test Plate	High Bond Strength	Low Bond Strength	Approximate Bond Strength
		lb. / inch of width	lb. / inch of width	lb. / inch of width
0	a	216	216	216
0	b	178	160	170
0	c	195	167	190
25	a	130	63	96
25	b	98	60	84
25	c	120	70	84
50	a	140	110	128
50	b	167	70	40
50	c	162	144	150
75	a	174	165	170
75	b	117	42	77
75	c	109	9	12

Table 9 - 90-degree peel test results for twenty-four inch spray distance.

C o n t r o l

Specimens

Test Period Days	Test Plate	High Bond Strength	Low Bond Strength	Approximate Bond Strength lb. / inch of width
		lb. / inch of width	lb. / inch of width	lb. / inch of width
0	a	170	90	120
0	b	162	95	108
0	c	140	100	120
25	a	120	0	0
25	b	180	90	132
25	c	160	88	110

Table 10 - 90-degree peel test results for control samples.

The control plates provided an initial bond that satisfied the design requirements as seen in Table (9). After 25 days of exposure, all three control plates exhibited some paint separation from the plate, and one plate failed entirely between the paint - NAB interface. The approximate bond strengths of the control samples are lower than the bond strengths of the thermally sprayed coatings, both initially and after environmental exposure as seen in Tables (5 - 9). This demonstrates that the thermal spray coating provided a better bonding surface for the paint than did a non-sprayed surface. The non-sprayed NAB plate results corresponded to data previously obtained on HY-80 non-sprayed steel plates tested by NSWC. The results obtained by NSWC, and by this project, indicate that a non-sprayed metal substrate cannot sustain an adequate bond with the paint coating over an extended period of time.

Initially, all four spray distances provided an adequate bonding surface for the paint - NAB interface with bond strengths well above the minimum requirement of 80 lbs. / linear inch of peel strip. All four bond strengths were similar in values, which was expected,

because the paint was the weakest link initially. The 12 and 18 inch spray distances provided the highest initial bond strength, with the 12 inch spray providing a slightly stronger bond as seen in Tables (6) and (7). The 12 and 18 inch spray distances were very effective because they created a surface with high porosity and minimal oxidation that allowed for good mechanical bonding with the paint, and strong inter-layer bonding within the thermally sprayed coating. The bond strength created by the six inch spray distance was lower than that of the 12 and 18 inch spray distances because of its minimal amount of porosity. The 24 inch spray distance also created a strong bond, though slightly weaker than the 12 and 18 inch spray distance created, due to the large amount of oxidation and porosity present in 24 inch spray coating. The large amount of oxidation and porosity created weak inter-layer bonding within the 24 inch thermally sprayed coating. All four spray distances provided a much stronger initial bond between the paint and substrate than was created by the non-sprayed control specimens. Once the test specimens were placed under cathodic protection in the salt water tanks, the primary adhering agent would eventually shift from the paint to the bond between the paint and the thermally sprayed coating, or to the thermally sprayed coating itself.

Figure (23) demonstrates that the bond strength of the 6 and 24 inch thermal spray plates greatly decays over time when exposed to cathodic protection in seawater. After 75 days the six and 24 inch spray test specimens had an average bond strength below 100 lbs / inch of width. The 24 inch spray distance had the lowest overall bond strength after 75 days, and suffered from catastrophic failure of the bonding between the thermal spray coating layers, as will be described in the next section. Throughout the testing, the 24 inch spray

distance specimens failed within the top layer of the thermally sprayed coating, vice failing between the paint - coating interface. This type of failure, compounded with the lack of overall bond strength, indicated that the 24 inch spray distance was not a viable distance to use when applying the NAB coating.

The six inch spray distance failed between the paint - coating interface, and the overall bond strength greatly decreased with time as seen in Figure (24). After 50 days, the six inch spray distance had an average bond strength below 100 lbs / inch of width, indicating that the six inch spray was not an effective distance for applying the thermal spray coating. The lack of bond strength was largely due to the minimal amount of porosity created on the surface at this spray distance, although the six inch spray distance performed better than the previous NSWC results.

The 12 inch spray distance provided an adequate average bond strength over the entire test period. After 50 days of exposure to seawater and cathodic protection, the overall bond strength was still above 100 lbs/ inch of width, as seen in Figure (25) and Table (6). After 75 days of exposure, the average bond strength was approximately 95 lbs / inch of width, which indicates that this distance provides an adequate mechanical bond between the paint - coating interface. With the overall bond strength decaying over time, it appeared as if the 12 inch spray distance might not provide an adequate mechanical bond if further exposed to a seawater environment under cathodic protection.

The 18 inch spray distance also created an adequate bond strength over the entire test period. Throughout the entire 75 days the average bond strength for this spray distance never went below 100 lbs/ inch of width as seen in Figure (26). The average bond strength

after 75 days of exposure was approximately 145 lbs / inch of width, well above the minimum requirement of 80 lbs/ inch of width. The overall high bond strength of the 18 inch spray distance indicated that this spray distance created an adequate mechanical bond between the paint - coating interface that minimized, or at least reduced, the effects of the cathodic protection system. The high bond strength after 75 days further suggests that this spray distance would continue to provide a good mechanical bond for the system under further exposure to seawater and cathodic protection.

An analysis of Figures (24) through (27) reveals interesting general characteristics about each spray distance. Figures (24) and (25) both show a gradual decrease in bond strength over time, although Figure (25) decreases at a slower rate than Figure (24). These figures indicate that the bond strength created by both the six inch and 12 inch spray distances decreased over time. The bond strength of the six inch spray distance appears to reach an asymptotic minimum at 50 days while the bond strength of the 12 inch spray distance appears to be approaching an asymptotic minimum at 75 days, with both minimums above the required 80 lb / linear inch bond strength. Figure (27), although showing numerical variations, appears to have an overall general decline in bond strength. It also appears that the bond strength of the 24 inch spray distance approaches an asymptotic minimum that is above the required 80 lb / linear inch. Figure (26) is very interesting because it appears that the overall bond strength reaches an minimum value at 25 days, and then begins to increase as the exposure time increases. This indicates that as the thermally sprayed coating at 18 inches may possibly become more effective as the exposure time to cathodic protection increased. Figure (26) indicates that the 18 inch spray distance provided the best surface for adhesion.

As Figure (23) indicates, the most efficient spray distance for creating a high bond strength was the 18 inch spray distance. Both the 6 inch and 24 inch spray distances proved inadequate after 50 and 75 days of environmental exposure under cathodic protection. Although the 12 inch spray distance proved efficient over the 75 day test period, the testing indicated that further exposure to seawater and cathodic protection would cause the bond strength to fall below acceptable levels.

The rise in average bond strength shown in Figures (24), (26), and (27) could have been caused by many things. Since only three specimens were evaluated for each testing cycle, a large statistical aberration could occur. Although the average bond strengths increased in Figures (24) and (27), the minimum bond strength steadily decreased, indicating that the overall bond strength was in fact decreasing. In Figure (26), the maximum, minimum, and average bond strengths increased. Aside from statistical aberration, this could have been caused by many factors ranging from the coating thickness to the amount of time between spraying and painting the plates. The rise in Figure (26) cannot be readily explained, therefore additional research must be done to confirm this phenomenon.

Finally, Figures (22) and (23) reveals that the thermally sprayed test specimens had an overall higher bond strength than the non-sprayed control specimens. Both the initial and 25 day average bond strength of the control specimens were significantly lower than the average bond strengths of the sprayed plates, proving the effectiveness of the thermally sprayed coating as a bonding agent.

SEM ANALYSIS

A Scanning Electron Microscope analysis was performed on various peel strips to determine whether or not the thermal sprayed coating failed during the peel test. During the peel tests two, distinctly different types of peel surfaces were created. The two surfaces indicated two different modes of failure and, therefore, reflected the reliability of each distinct spray distance. The first peel surface discovered is seen in Figure (28).



Figure 28 - typical view of bond failure w which occurred between the paint and urethane interface during the 90-degree peel test.

This surface represents the ideal peel surface desired due to the minimal amount of visible paint on the peel strip. The minimal amount of paint showing on the peel surface indicates that the failure occurred between the urethane - paint interface, an interface that is not controlled by the thermal sprayed coating.

The thermally applied coating effects the bonding that occurs between the paint and the substrate, and if the thermally applied coating held, then the mode of failure will occur between the paint and urethane. This peel surface indicates that the thermally applied coating was able to minimize the effects of the cathodic protection, and maintain the overall bond strength and integrity of the chemical bond between the NAB and 2842 series paint. Multiple elemental x-ray analysis were performed on two of the peel strips to ensure that the mode of failure was consistent throughout the entire peel strip. The results can be seen in Table (11) and a typical x-ray analysis in Figure (29).

Table 11 -Weigh percent composition of elements on a sample peel strip which failed at the paint - urethane interface.

Element	Weight%			Average Weight%
	Run 1	Run 2	Run 3	
Na	2.41	2.30	2.52	2.41
Al	5.73	5.65	5.74	5.71
Si	35.84	38.23	36.63	36.90
Cl	11.76	11.09	13.49	12.11
K	5.63	4.57	6.01	5.40
Ca	5.32	3.31	4.38	4.34
Fe	33.31	35.03	31.23	33.19
Ni	0.00	0.00	0.00	0.00
Cu	0.00	0.00	0.00	0.00

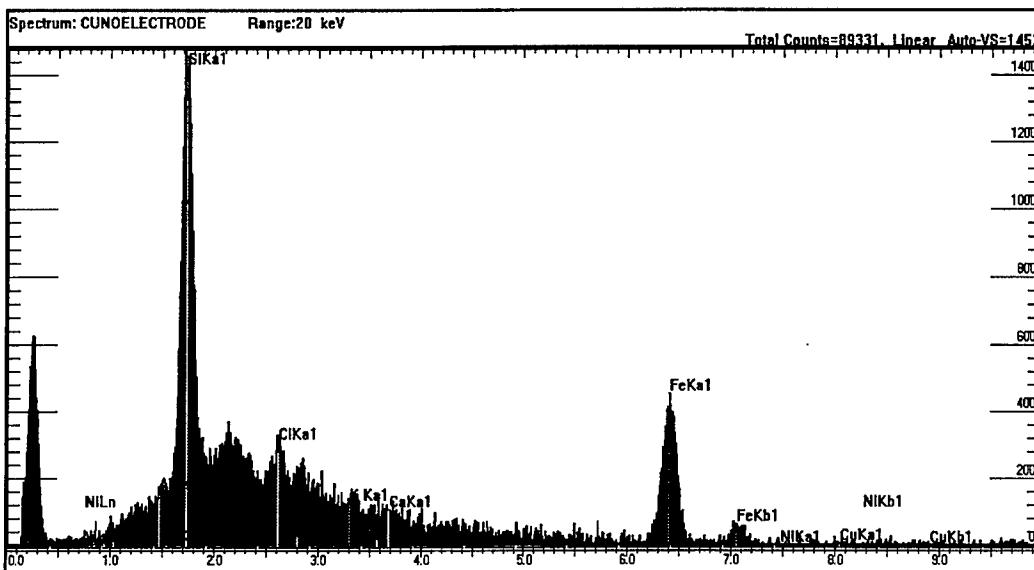


Figure 29 - typical spectrum (20KeV accelerating voltage) of a peel surface with a bond failure between the paint and urethane interface. Notice the lack of copper and nickel peaks.

As Table (11) and Figure (29) reveals, there is no copper or nickel present on the peel strip surface. This indicates that thermal sprayed coating did not fail during the testing of the specimen. The specimens which contained this type of peel surface are shown in Table (12).

Table 12 - Test specimens which failed at the paint - urethane interface.

Spray Distance	Exposure				
	Time	0 Day	25 Day	50 Day	75 Day
6 inches	a,b,c	c	a,b,c	a,b,c	
12 inches	a,b,c	a,b	a,b,c	a,b,c	
18 inches	a,b,c	a,b,c	a,b,c	a,b,c	
24 inches	a,b,c	NONE	a	a	

As shown in Table (12), both the 12 and 18 inch thermal spray distance proved successful over the entire test period of 75 days. As previously shown in the peel test, these two distances provide the best surface characteristics for creating and maintaining a strong mechanical bond between the paint and the NAB substrate.

The second peel surface discovered, was one that was created through the internal failure of the thermally sprayed coating. The thermally sprayed coating failed at the surface of the paint - metal interface. This failure was due to corrosion that occurred within the coating, with the large pores serving as corrosion concentrators. The thermally sprayed coating can be seen on the peel strip, as well as the paint which remained adhered to the coating, as seen in Figure (30).



Figure 30 - typical view of a peel surface which failed between the paint and NAB interface during the 90-degree peel test.

The visual verification that the paint remained adhered to the thermally sprayed coating indicates that the mechanical bond between the paint - NAB interface was still sufficiently strong, and that the failure occurred within the thermally sprayed coating.

X-ray analysis was performed on multiple areas of the test specimen to confirm that the thermally sprayed coating had actually failed internally at the surface. It was found that copper, nickel, and aluminum were all present in this inspection as seen in Table (13). Therefore, the mode of failure was the internal failure of the thermally sprayed coating. A typical x-ray analysis spectrum of this type of peel surface can be seen in Figure (31).

Table 13 - Weight percent of elements on a test peel strip which failed at the paint - NAB coating interface.

Element	Weight%			Average
	1	2	3	
Al	9.24	11.50	11.13	10.62
Si	39.12	38.76	36.96	38.28
Cl	13.52	15.94	12.14	13.87
K	6.36	7.22	6.20	6.59
Ca	4.61	6.01	4.64	5.09
Fe	16.75	14.56	16.72	16.01
Ni	2.05	1.19	3.51	2.25
Cu	8.35	4.82	8.71	7.29

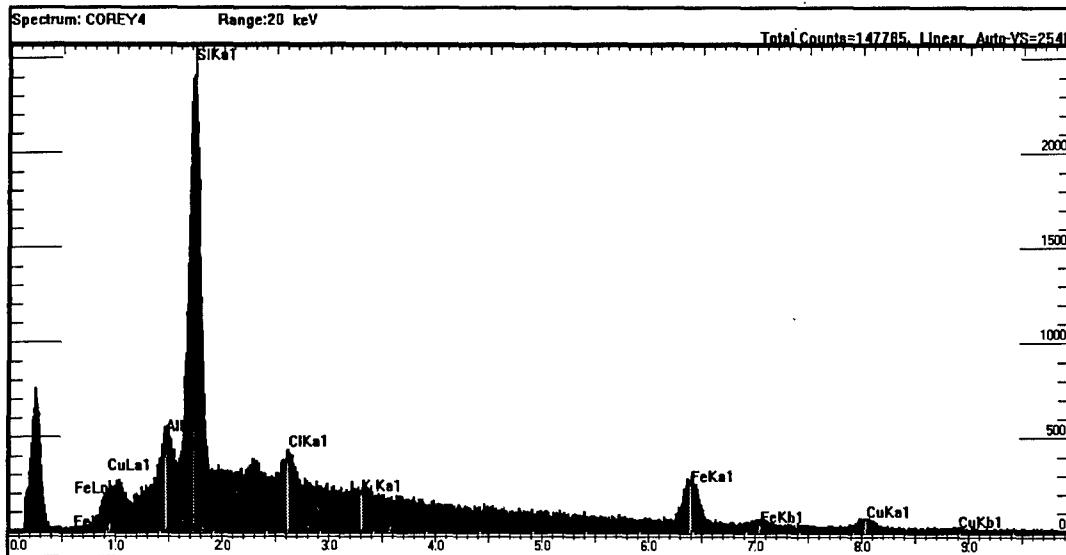


Figure 31 - typical spectrum (20KeV accelerating voltage) of a peel surface with a bond failure between the paint and NAB interface. Notice the copper and nickel peaks.

Nickel, aluminum, and copper are clearly visible in the spectrum and in the table, thus verifying the visual inspection of the peel surface. These findings confirm that the mode of failure was failure of the thermally sprayed coating. This type of failure occurred catastrophically on the test specimen. This mode of failure was unacceptable for the conditions under which the propeller blade will be required to operate, and thus eliminated all spray distances which exhibit this characteristic. The spray distances which experienced this mode of failure are summarized in Table (14).

Table 14 - Test specimens which failed at the paint - NAB coating interface.

Spray Distance	Exposure			
	Time			
	0 Day	25 Day	50 Day	75 Day
6 inches	NONE	a,b	NONE	NONE
12 inches	NONE	NONE	NONE	NONE
18 inches	NONE	c	NONE	NONE
24 inches	NONE	a,b,c	b,c	b,c

From the two types of peel surfaces evaluated under the SEM, it was determined that the 24 inch spray distance created an unacceptable coating surface. On the other hand, both the 12 and 18 inch spray distances proved effective in meeting the requirements of this project.

CONCLUSIONS AND RECOMMENDATIONS

From this investigation it was determined that a thermally sprayed coating using the Arc Wire Spray system can produce an adequate surface that can overcome, or at least reduce the deterioration of a urethane coated propeller caused by the impressed current cathodic protection system. Additionally, it was determined that a spray distance of 18 inches produced the best surface characteristics, system life, and overall system bond strength.

The surface characteristics of the 18 inch thermal sprayed coating were 15.67% porosity, 15.57% oxidation, at least a 75 day successful life in the presence of cathodic protection, and an average bond strength of 147.3 lb / linear inch of width after 75 days of exposure. The porosity was high enough, and the oxidation low enough, in the 18 inch sprayed coating to allow for strong mechanical bonding, while also being able to support the applied loading conditions on the coating itself.

Additionally, the 12 inch spray distance was proven to meet the project requirements, but was not as effective as the 18 inch spray distance. The average bond strength of the 12 inch spray distance was 95 lb / linear inch of width after 75 days and appeared to be decreasing with time. The 12 inch spray did not possess a high enough porosity, 13.75%, to create a strong enough mechanical bond to provide long lasting adhesion between the paint and the NAB substrate.

The results also revealed that a six inch spray distance, although adequate, did not provide the desired surface characteristics. The six inch spray distance created a surface with the characteristics of 10.67% porosity, 10.78% oxidation, and a bond strength of 97.8

lb / linear inch of width at 75 days. The low porosity was due to the close proximity of the arc wire gun nozzle to the plates and would not allow for adequate mechanical bonding to occur. Minimal cooling would occur between the nozzle and substrate, so that the metal hitting the plate would partially remelt the previous coating layers and mix with them, filling in the previously created pores. Due to this, it was concluded that the AWS coating should not be applied at any distance less than six inches.

Finally, the 24 inch spray distance produced a highly porous surface, 17.19%, with large pores, but the mechanical bond created between the paint and coating did not hold. This loss of the mechanical bond was possibly due to corrosion that occurred within the large pores of the thermally sprayed coating. As the corrosion formed, it weakened the bond within the thermally applied coating to the point that it failed before the paint - NAB interface failed. This led to catastrophic failure on many of the plates tested at this spray distance. From this it was concluded that the AWS coating should be applied at distances under 24 inches, as larger distances would have created large pores and more oxidation, leading to even worse behavior.

Despite the success of this project, it is highly recommended that retesting of this process be performed due to experimental anomalies and inconsistencies. In conducting these retests, only the 12 and 18 inch spray distances should be evaluated, and the exposure time should be increased to six months with one month peel test evaluations performed. In order to overcome inconsistencies in the urethane coating thickness, a more accurate mold should be created, so that all the urethane peel strips remain constant throughout the experiment. The thermal spraying should also be performed more accurately to maintain a

constant spray distance from the plates. With these recommendations, a retest should be performed to validate the results obtained in this experiment.

Although the AWS coating greatly increased the life of the urethane coated system, it is only a part of the final solution. The creation of a mechanical bond, along with the increased chemical adhesion between the paint and the substrate, has proven to be an effective mechanism to overcome the degradation of the bond strength that occurs within the system due to the cathodic protection system. The enhanced bonding proved adequate, but the overall system bond strength decreased as the exposure time increased. In order to construct a more reliable system, a better paint system that has both good adhesion properties and good corrosion resistance properties, must be developed. Once a paint system of this type is developed, it should be tested in conjuncture with the AWS applied coating for overall bond strength and life expectancy under operating conditions.

The idea of a urethane coated propeller is a reachable goal. With further research and experimentation, the final problems should be resolved, and this technology should be ready to use in the VIRGINIA Class submarine propeller program, as well as the rest of the maritime industry.

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